

Catalytic Hydroxylation of Polyethylenes

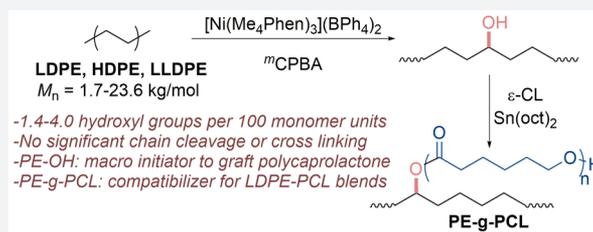
Ala Bunesco,[†] Sunwoo Lee,^{†,‡} Qian Li,[†] and John F. Hartwig^{*,†}

[†]Department of Chemistry, University of California, Berkeley, California 94720, United States

[‡]Department of Chemistry, Chonnam National University, Gwangju 61186, Republic of Korea

S Supporting Information

ABSTRACT: Polyolefins account for 60% of global plastic consumption, but many potential applications of polyolefins require that their properties, such as compatibility with polar polymers, adhesion, gas permeability, and surface wetting, be improved. A strategy to overcome these deficiencies would involve the introduction of polar functionalities onto the polymer chain. Here, we describe the Ni-catalyzed hydroxylation of polyethylenes (LDPE, HDPE, and LLDPE) in the presence of ^mCPBA as an oxidant. Studies with cycloalkanes and pure, long-chain alkanes were conducted to assess precisely the selectivity of the reaction and the degree to which potential C–C bond cleavage of a radical intermediate occurs. Among the nickel catalysts we tested, [Ni(Me₄Phen)₃](BPh₄)₂ (Me₄Phen = 3,4,7,8-tetramethyl-1,10-phenanthroline) reacted with the highest turnover number (TON) for hydroxylation of cyclohexane and the highest selectivity for the formation of cyclohexanol over cyclohexanone (TON, 5560; cyclohexanol/(cyclohexanone + ε-caprolactone) ratio, 10.5). The oxidation of *n*-octadecane occurred at the secondary C–H bonds with 15.5:1 selectivity for formation of an alcohol over a ketone and 660 TON. Consistent with these data, the hydroxylation of various polyethylene materials by the combination of [Ni(Me₄Phen)₃](BPh₄)₂ and ^mCPBA led to the introduction of 2.0 to 5.5 functional groups (alcohol, ketone, alkyl chloride) per 100 monomer units with up to 88% selectivity for formation of alcohols over ketones or chloride. In contrast to more classical radical functionalizations of polyethylene, this catalytic process occurred without significant modification of the molecular weight of the polymer that would result from chain cleavage or cross-linking. Thus, the resulting materials are new compositions in which hydroxyl groups are located along the main chain of commercial, high molecular weight LDPE, HDPE, and LLDPE materials. These hydroxylated polyethylenes have improved wetting properties and serve as macroinitiators to synthesize graft polycaprolactones that compatibilize polyethylene–polycaprolactone blends.



INTRODUCTION

The synthesis of functionalized polyolefins is a synthetic goal that has been widely sought. The most straightforward way to incorporate polar functionality along the main chain is the copolymerization of unfunctionalized alkenes with polar monomers.^{1,2} Free-radical copolymerization of ethylene with polar vinyl monomers (vinyl acetate, methyl acrylate, acrylonitrile, etc.) is well-known and conducted commercially, but these polymerizations form materials with high polydispersity index, a high degree of branching, and a nonuniform distribution of the polar functional groups in the polymer chain.³ Thus, much research has been devoted to the catalytic copolymerization of ethylene or α-olefins with monomers containing polar functional groups on the alkene.^{4–9} However, despite a half-century of research on this topic, these reactions do not occur with activities and levels of incorporation that are practical, and the molecular weights of the copolymers are typically lower than those of homopolymer. The lower molecular weight of polymer results from the poisoning of the complexes that catalyze coordination polymerizations by the polar monomer.^{4,5,9}

The direct functionalization of polyolefins could be an alternative route to materials containing polar functional groups.^{10–14} This approach to functionalized polyolefins has

several advantages over radical and catalytic copolymerization. For example, one can introduce polar functionality into materials that possess molecular weights, tacticity, and microstructure derived from established systems that catalyze the polymerization of unfunctionalized olefins with high activity, stereoselectivity, and incorporation of α-olefin comonomers. In addition, the degree of functionalization should be controlled by the reaction stoichiometry, and a random distribution of functional groups on the polymer backbone could be achieved.

Most methods for the functionalization of polyolefins occur by generating free alkyl radicals by abstraction of a hydrogen atom from the polymer chain under harsh reaction conditions.¹¹ Thus, the current functionalizations of polyethylene occur with competing, undesired processes, such as scission of the polymer chain and cross-linking of the chains. These side reactions compromise the mechanical properties of the material, and this strategy has led to few commercial processes.^{15–17} The oxidation of polyethylenes that occurs with concomitant C–C bond cleavage is conducted industrially to

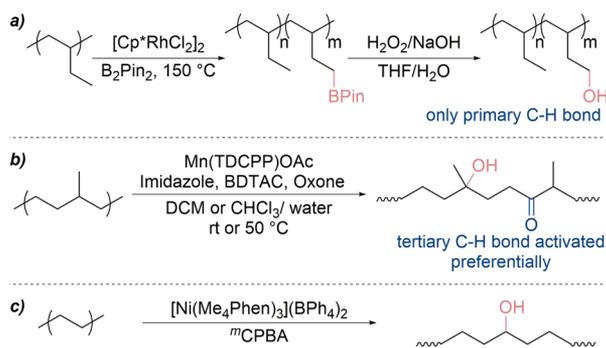
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obtain oxidized polyethylene waxes containing a mixture of aldehyde, alcohol, and carboxylic acid functionalities.^{18–21}

An alternative to free-radical functionalization of polyolefins is metal-catalyzed C–H bond functionalization.^{9,22} However, few examples of metal-catalyzed functionalizations of polyolefins have been reported.^{10,23–25} Hillmyer and Hartwig reported the Rh-catalyzed borylation of polyethylene (PEE) and polypropylene (PP) with bis(pinacolato)diboron (B₂Pin₂), followed by oxidation with hydrogen peroxide to generate a material containing hydroxyalkyl side chains (Scheme 1a).^{26–28} However, these reactions do not occur at

Scheme 1. Metal-Catalyzed Hydroxylation of Polyolefins^a



^a(a) Rh-catalyzed borylation/oxidation reaction. (b) Mn-catalyzed hydroxylation. (c) This work: Ni-catalyzed hydroxylation.

the secondary C–H bonds of polyethylene. In addition, Hillmyer and co-workers reported the direct oxidation of PEP (poly(ethylene-*alt*-propylene)) catalyzed by a manganese(III)–porphyrin complex (manganese(III) *meso*-tetra-2,6-dichlorophenylporphyrin acetate, Mn(TDCPP)OAc), imidazole, a phase transfer agent (benzyltrimethyltetradecylammonium chloride, BDTAC), and oxone (Scheme 1b).^{29,30} However, this oxidation reaction occurred preferentially at tertiary C–H bonds.

We report an approach to the hydroxylation of polyethylene without competing chain scission or cross-linking based on nickel-catalyzed oxidations of C–H bonds.^{31–37} Our initial studies on linear alkanes revealed the most active nickel catalysts and evidence that the processes occur without typical side reactions resulting from free alkyl radicals. Application of this system to the functionalization of a range of polyethylenes with varying molecular weights and alpha-olefin comonomers showed that the oxidation occurred selectively at secondary C–H bonds of these polymers and, in contrast to previous uncatalyzed hydroxylation of polyethylene, occurred without competing chain scission or cross-linking.

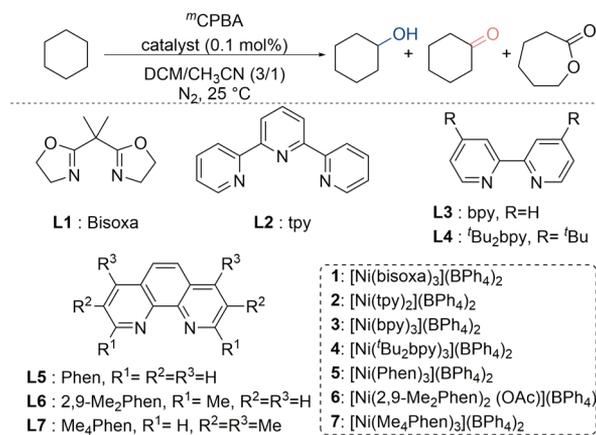
RESULTS AND DISCUSSION

Oxidation of Alkanes. The combination of nickel catalysts and *m*CPBA (*meta*-chloroperoxybenzoic acid) has been shown to oxidize cyclohexane to form alcohols over ketones with high turnover numbers.^{31–39} Although such reactions are far from oxidations of polyolefins, we explored the potential of this type of system to catalyze the hydroxylation of polyethylenes. Translation of this reactivity to polyolefins would require improvements to the catalyst, analysis of selectivity, and careful studies on potential side reactions that could lead to chain cleavage and cross-linking. Chain cleavage could occur by abstraction of a hydrogen atom to form an alkyl radical or by

oxidation of the ketone to form esters that can be a site for chain cleavage. To identify appropriate nickel catalysts for the oxidation of polyethylene, we first tested reactions of light alkanes catalyzed by a series of nickel complexes. The most active and selective of these catalysts would then be applied to the oxidation of a series of polyethylene materials.

Ni complexes 1–7 (see Table 1) were synthesized from Ni(OAc)₂·4H₂O and bidentate or tridentate nitrogen-based

Table 1. Oxidation of Cyclohexane by Ni Complexes^a



entry	catalyst	C ₆ H ₁₁ OH:C ₆ H ₁₀ (O):ε-CL ^b	TON ^c
1 ^d		traces	
2	1	17.4:1: 2.7	617
3	2	13.6:–:1	132
4	3	14.2:1:1.7	592
5	4	5.9: traces:1	562
6	5	15.3:1:1.8	589
7	6		60
8	7	26.4:1:4.3	621
9	8 ^e	15.9:1:2.7	569
10 ^f	7	10.5:traces:1	5560
11 ^f	8 ^e	5.4:traces:1	5340
12 ^g		5.3:traces:1	21% ^h

^aStandard conditions: Cyclohexane (7.5 equiv), *m*CPBA (1.0 equiv), DCM/CH₃CN (3:1, 0.5 M) under N₂ atmosphere for 19 h; the reactions were conducted in closed vials with a Teflon-lined cap.

^bDetermined by ¹H NMR spectroscopy with *n*-C₁₂H₂₆ as internal standard. ^cTON = (alcohol + ketone + ε-CL)/catalyst. ^dWithout catalyst. ^e[Ni(TPA(OAc)(H₂O))(BPh₄)₂], TPA = tris(2-pyridylmethyl)amine. ^f0.01 mol % of Ni catalyst, DCE, 50 °C. ^gWithout catalyst, DCE, 50 °C. ^hYield of alcohol + yield of ε-CL based on *m*CPBA.

ligands, such as those from bisoxazoline (bisoxa), terpyridine (tpy), bipyridine (bpy), and phenanthroline (phen) structures. The Ni complexes 1–7 were characterized by high-resolution mass spectrometry (HRMS), cyclic voltammetry, elemental analysis, infrared spectroscopy (IR), and ultraviolet–visible (UV–vis) spectroscopy.^{31,32,40–42} (see the Supporting Information). Compound 7 was characterized by single-crystal X-ray diffraction (see the Supporting Information). The Ni complex 7 exhibits a distorted octahedral geometry that is similar to those of previously reported [Ni(bipy)₃]²⁺, [Ni(phen)₃]²⁺, and [Ni(tpy)₂]²⁺ structures possessing different counteranions.^{40,43,44}

The relative activity of nickel catalysts 1–7 for the oxidation of C–H bonds was assessed first by conducting reactions with

cyclohexane. Table 1 shows the results of the reactions of cyclohexane (7.5 equiv) with ^mCPBA (1.0 equiv) in a mixture of dichloromethane and acetonitrile in the presence of the nickel complexes at room temperature under nitrogen. The oxidation of cyclohexane catalyzed by [Ni(Me₄Phen)₃](BPh₄)₂ (7) provided cyclohexanol in the highest yield among reactions catalyzed by this set of complexes (52%) with high selectivity for the formation of alcohol versus carbonyl compounds (ratio of alcohol:ketone:ε-caprolactone (ε-CL) = 26.4:1:4.3, Table 1, entry 8). The reactions catalyzed by complexes of other bidentate pyridine ligands occurred with lower selectivity for the alcohol or with lower TON.

The reaction conducted with a loading of catalyst 7 of 0.01 mol % in dichloroethane (DCE), at 50 °C, occurred with the highest TON and selectivity for the formation of cyclohexanol over cyclohexanone (TON, 5560; cyclohexanol/(cyclohexanone + ε-caprolactone) = 10.5; Table 1, entry 9). The reactions with the previously reported catalyst 8 based on tris-pyridylmethylamine occurred with selectivity for alcohol over carbonyl compound that was lower than that of catalyst 7 by a factor of 2 (see Table 1, entry 11). As presented later, this higher propensity to form esters parallels a higher degree of polymer chain cleavage during the oxidation of polyethylene.

The relative activity of the catalysts generated from various nitrogen-based ligands can be rationalized in terms of the number of donating atoms, steric properties, and electron-donating abilities. Dissociation of a ligand from the octahedral nickel complex would precede the reaction with ^mCPBA.^{38,39,45,46} Catalyst 2 containing the terpy ligand would be less prone to dissociate a ligand to coordinate the ^mCPBA.^{47,48} The reactions with catalysts containing electronically varied phenanthroline ligands (see Table S1) showed that those containing electron-donating groups (–Me, –N(iPr)₂, –OMe) on the phenanthroline ligands were much more active than those containing electron-withdrawing groups (–Cl and –Br). The reactions catalyzed by the analogous complexes generated from phenanthrolines containing electron-withdrawing groups, such as 3,4,7,8-tetrabromo-1,10-phenanthroline or 4,7-dichloro-1,10-phenanthroline, formed only traces of cyclohexanol. An increase in the steric properties of the ligand decreased the catalyst activity. Ligands containing substituents at the 2 and 9 positions (–^tBu, –CO₂H, –CN) generated catalysts that form the oxidized cyclohexane in low yield.

The reaction of cyclohexane with a series of alternative oxidants was conducted with [Ni(Me₄Phen)₃](BPh₄)₂ as catalyst. These oxidants included hydrogen peroxide, cumene hydroperoxide, *tert*-butyl hydroperoxide, *tert*-butyl peroxybenzoate, peracetic acid, and peroxybenzoic acid. Among this set, only reactions with the peroxyacids furnished oxidation products, and the reactions of cyclohexane with ^mCPBA as oxidant furnished cyclohexanol in the highest yield.

Having identified conditions for the selective hydroxylation of cyclohexane with thousands of turnovers, we studied the analogous reactions of a pure, long-chain alkane, *n*-octadecane, to test whether these reactions of cyclohexane would translate to the oxidations of a long-chain linear alkane. Important for applications to the functionalizations of polyethylene, these reactions of pure *n*-octadecane could be scrutinized for the formation of shorter-chain products that would result from C–C bond cleavage

We conducted the hydroxylations of octadecane at 80 °C because low molecular weight PE is soluble in DCE at this temperature, making the conditions relevant to anticipated

studies on polyethylene. At these higher temperatures of 65–80 °C, ^mCPBA is known to oxidize cyclohexane in the absence of a metal catalyst.⁴⁹ To evaluate the impact of a potential background hydroxylation of a linear alkane, the oxidation of *n*-octadecane was conducted in the presence and absence of Ni catalyst 7 (Table 2, entries 1 and 2). The nickel-catalyzed

Table 2. Oxidation of *n*-Octadecane by ^mCPBA with and without [Ni(Me₄Phen)₃](BPh₄)₂

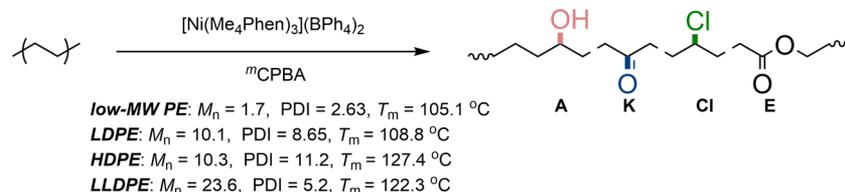
entry	variation from standard conditions ^a	A ₁₈ :K ₁₈ :Cl ₁₈ :E ₁₈ (%) ^{b,c}
1		41:21:20:–
2	no Ni catalyst	18:4:10:15
3	PhCO ₃ H	30:13:16:–
4	CH ₃ CN	21:31:8:–
5	PhCO ₃ H, CH ₃ CN	28:35:–:–
6	^m C ₁₈ H ₃₈ : ^m CPBA = 5:1	62:4:5:– ^d

^aStandard conditions: ^mC₁₈H₃₈:^mCPBA:[Ni(Me₄Phen)₃](BPh₄)₂ = 1:4:4 × 10^{–3}, DCE (0.1 M), 80 °C, N₂, 3 h; the reactions were conducted in closed vials sealed with a Teflon-lined cap. ^bAmount of alcohol, ketone, chloroalkyl, and ester functionalities based on ^mC₁₈H₃₈. ^cDetermined by ¹H NMR spectroscopy using CH₃NO₂ as internal standard. ^d^mC₁₈H₃₈:^mCPBA:[Ni(Me₄Phen)₃](BPh₄)₂ = 5:1:10^{–3}, yields based on ^mCPBA.

oxidation of *n*-octadecane gave products from hydroxylation of the secondary C–H bonds as the major product (41% yield), as determined by ¹H NMR spectroscopy (Table 2, entry 1). These reactions also generated a side product from chlorination of the alkane.

The oxidation of octadecane occurred in the absence of Ni at this temperature. However, this uncatalyzed reaction occurred with a yield and selectivity that were lower than those of the reactions conducted in the presence of the Ni catalyst. This reaction formed only 18% of the alcohol and 4% of the ketone. Most striking, we found that the reaction in the absence of nickel generated almost as much product resulting from Baeyer–Villiger oxidation of the ketones to the corresponding esters as product from simple hydroxylation (Table 2, entry 1 vs 2). The reaction catalyzed by nickel formed only trace amounts of the ester; again, this larger amount of ester correlates with the degree of chain cleavage of the polyethylenes.

Several possible compounds could be the source of chlorine, including the solvent (DCE), ^mCPBA, or chlorobenzene formed by decarboxylation of *meta*-chlorobenzoic acid (^mCBA). To trace the origin of the chlorine, a series of control experiments were conducted. First, ^mCPBA was replaced with peroxybenzoic acid (PBA) (Table 2, entry 3 vs entry 1). The reaction with PBA formed chlorinated octadecanes in 16% yield. This result suggests that DCE is the major source of chlorine atoms under the standard conditions. Second, the oxidation reaction was conducted in acetonitrile with ^mCPBA and PBA (Table 2, entries 4 and 5). The amount of chlorooctadecanes formed from the reaction with ^mCPBA as oxidant in acetonitrile was lower (8%) than that from the reaction in DCE (20%), but some product from chlorination was still observed (Table 2, entry 5). These results suggest that both chlorobenzene and ^mCPBA can be sources of chlorine in the chlorination process that competes with oxidation. The

Table 3. Oxidation of Polyethylene by ^mCPBA with and without [Ni(Me₄Phen)₃](BPh₄)₂

entry	notes on conditions ^a	TF ^b	A:K:Cl:E ^c	(M_w , M_n , PDI) ^d	T_m (°C) ^e
Low MW PE					
Condition A: Ratio PE monomer: ^m CPBA:[Ni(Me ₄ Phen) ₃](BPh ₄) ₂ = 100:7.2:7.2 × 10 ⁻³ , [PE Monomer] = 11.0 M, DCE 80 °C					
1	condition A	2.6	86:7:7:–	4.0, 1.8, 2.21	95.7
2	[PE monomer] = 22.0 M	3.0	88:5:5:2	4.1, 1.9, 2.14	95.0
3	[PE monomer] = 1.1 M	2.0	70:6:24:–	4.4, 1.9, 2.37	103.4
4	PE monomer: ^m CPBA:[Ni(Me ₄ Phen) ₃](BPh ₄) ₂ = 100:10.8:10.8 × 10 ⁻³	3.6	85:9:6:–	4.2, 2.0, 2.11	91.6
5	PE monomer: ^m CPBA:[Ni(Me ₄ Phen) ₃](BPh ₄) ₂ = 100:14.5:14.5 × 10 ⁻³	4.8	80:10:8:2	4.3, 2.1, 2.08	88.2
6	no catalyst	2.1	70:4:10:16	3.8, 1.7, 2.27	89.4
LDPE					
Condition B: Ratio PE monomer: ^m CPBA:[Ni(Me ₄ Phen) ₃](BPh ₄) ₂ = 100:14.5:14.5 × 10 ⁻³ , [PE Monomer] = 11.0 M, DCE, 90 °C					
7	condition B	4.0	75:11:14:–	84.4, 10.2, 8.28	105.2
8	Ni catalyst 8	2.9	58:12:9:21	62.9, 8.3, 7.56	112.2
9	no catalyst	3.9	28:20:3:49	15.3, 4.8, 3.2	96.0
HDPE					
Condition C: Ratio PE monomer: ^m CPBA:[Ni(Me ₄ Phen) ₃](BPh ₄) ₂ = 100:14.5:29.0 × 10 ⁻³ , [PE Monomer] = 2.8 M, DCE/1,2,4-TCB(3/1), 80 °C					
10	condition C	2.3	60:19:21:–	127.7, 10.8, 11.86	125.9
11	no catalyst	0.7	14:28:–:58	55.3, 8.6, 6.41	126.6
LLDPE					
Condition D: Ratio PE monomer: ^m CPBA:[Ni(Me ₄ Phen) ₃](BPh ₄) ₂ = 100:14.5:14.5 × 10 ⁻³ , [PE Monomer] = 2.8 M, DCE/1,2,4-TCB(1/1), 80 °C					
12	condition D	2.8	68:16:16:–	117.3, 19.4, 6.04	121.6
13	no catalyst	2.1	17:22:18:43	25.2, 7.4, 3.42	122.5

^aReactions conducted under N₂ atmosphere for 3 h in closed vials sealed with a Teflon-lined cap. ^bTF = 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. ^cRatio of alcohol (A), ketone (K), and chloroalkyl (Cl) functionalities calculated from the ¹H NMR spectrum. ^d M_w , M_n , PDI of functionalized polyethylene. ^eMelting temperature was 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. PDI = polydispersity index, M_w/M_n . DCE = 1,2-dichloroethane. 1,2,4-TCB = 1,2,4-trichlorobenzene.

reaction with PBA in acetonitrile did not form any chloroalkane, due to the absence of a chlorine-containing reaction component, but the ratio of alcohol to ketone was lower than it was from reactions in DCE. Ultimately, we minimized the formation of alkyl chloride by running the reaction at higher concentration, lower temperature, or higher ratios of *n*-octadecane to ^mCPBA. With *n*-octadecane as the limiting reagent in the Ni-catalyzed oxidation reaction, the ratio of (alcohol + ketone) to chloroalkane was 3.1 (Table 2, entry 1). However, with ^mCPBA as limiting reagent, as would be the case in the oxidation of polyethylenes, the ratio of (alcohol + ketone) to chloroalkane was 13.2 (Table 2, entry 6).

Oxidation of Polyethylenes. The hydroxylation reactions of cyclohexane and *n*-octadecane with the most active and selective catalyst for light alkanes were then applied to the hydroxylation of polyethylenes of varying molecular weights and microstructures (Table 3). The number of alcohol, ketone, and chloroalkyl functional groups were evaluated by ¹H NMR spectroscopy. The ¹H spectrum (TCE-*d*₂) of the oxidized polymer contained three new signals with chemical shifts that corresponded to the hydrogens α to the hydroxyl group (CH_a–OH, 3.60–3.67 ppm), α to the chloride (CH_c–Cl 3.90–3.97 ppm), and α to the carbonyl group (CH_{2k}–C(O)–CH_{2k}, 2.40–2.46 ppm). In some cases, two peaks that are characteristic of an ester group were observed at 4.13–4.19 ppm (C(O)–OCH_{2e}) and 2.33–2.39 ppm (CH_{2e}–C(O)–O) (see Figure

S2). The initial studies were conducted with low molecular weight polyethylene (Aldrich, $M_w = 4.3$ kg/mol, $M_n = 1.7$ kg/mol, polydispersity index (PDI) = 2.63) because this material is soluble in DCE at 80 °C.

To determine the effects of the reaction parameters on the degree of oxidation of this polymer, we conducted the Ni-catalyzed oxidation of low molecular weight polyethylene with varied temperatures, concentrations, and stoichiometry (ratio PE to oxidant). The degree of functionalization of the polyolefin (functional groups per 100 ethylene units) was higher at higher temperature. However, the selectivity for formation of the alcohol over alkyl chloride was lower for reactions conducted at higher temperature (see Table S4). Fortunately, both the efficiency of the oxidant and the selectivity for hydroxylation were higher for reactions run at higher concentration (see Table 1, entries 1–3). At 1.1 M concentration of monomer, the number of functional groups per 100 monomer units was 2.0 and the ratio of alcohol to chloride was 3:1 (see Table 3, entry 3 vs entry 2), but at 22.0 M concentration of monomer, the number of functional groups per 100 monomer units was 3.0, and the selectivity for alcohol to chloride was as high as 18:1.

The reaction of low molecular weight polyethylene with varying ratios of ^mCPBA to monomer allowed the number of hydroxyl groups introduced onto the polymer backbone to be tuned (see Table 3, entries 1, 4, and 5). For instance when the

ratio of monomer to oxidant was 100:7.2, 2.6 functional groups per 100 ethylene units were introduced (Table 3, entry 1), and when the ratio of monomer to oxidant was a factor of 2 smaller (100:14.5), roughly twice the number of functional groups per 100 ethylene units (4.8) were introduced (Table 3, entry 5).

The reaction in the absence of Ni catalyst formed polymer containing a lower degree of functionalization and with lower selectivity for introduction of hydroxyl versus ester functionality. This reaction with the low molecular weight polyethylene model resulted in the introduction of only 2.1 functional groups per 100 monomer unit. Moreover, 16% of the functionality present in the product of the uncatalyzed oxidation of polyethylene was ester groups.

To assess the ability of these conditions developed with pure alkanes and a model polyethylene to functionalize high molecular weight polyethylenes having different microstructures, the reaction was conducted with commercial 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). To functionalize these materials, the reaction conditions developed for functionalization of low molecular weight polyethylene (ratio of ethylene monomer:^mCPBA:[Ni(Me₄Phen)₃](BPh₄)₂ = 100:14.5:14.5 × 10⁻³ in DCE, 11.0 M, 80 °C) needed to be adjusted because of the lower solubility of higher molecular weight polyethylenes in DCE. To achieve the appropriate solubility, three approaches were employed: (1) adding a cosolvent (1,2-dichlorobenzene or 1,2,4-trichlorobenzene); (2) conducting the reaction at lower concentrations; and (3) conducting the reactions at higher temperatures.

The results for the functionalization of the various polyethylenes are shown in entries 7–13 of Table 3. The reactions with low-density polyethylene LDPE at 11.0 M concentration and 90 °C led to the introduction of 4.0 functionalities per 100 monomer units with 75% of these functional groups being an alcohol (Table 3, entry 7). The reactions of HDPE and LLDPE in a mixture of DCE and 1,2,4-TCB generated products containing 2.3 and 2.8 functionalities per 100 ethylene units of the polymer backbone, with the alcohol representing 60% and 68% of the total functionality, respectively (Table 3, entries 10 and 12).

The reactions of LDPE, HDPE, and LLDPE were also conducted in the absence of Ni catalyst (Table 3, entries 9, 11, and 13). In all three cases, ¹H NMR analysis of the oxidized materials showed that the selectivity and efficiency of the reactions in the absence of nickel were significantly different from those conducted in the presence of the nickel catalyst (see Figures S2b vs S2c). For instance, only 0.7 functionalities per 100 monomer units were introduced into HDPE in the absence of catalyst, whereas 2.3 functionalities per 100 monomer units were introduced in the presence of the Ni catalyst (Table 3, entry 11 vs 10). Moreover, the major functionality introduced by the uncatalyzed reaction was the ester (58% of the total amount of functionalities), whereas the major functionality introduced by the nickel-catalyzed reaction was the alcohol (60% of the total amount of functionalities).

In addition, the M_w , M_n , and PDI values measured by GPC (gel permeation chromatography) for the functionalized polyethylenes from reactions conducted in the presence of catalyst were different from those of functionalized polyethylenes from reactions conducted in the absence of catalyst.

As shown in Table 3, the M_w , M_n , and PDI values of the polymer generated by nickel-catalyzed oxidation were nearly identical to those of the starting, unfunctionalized polyethylene. In contrast, the M_w , M_n , and PDI values of the functionalized materials formed by the uncatalyzed oxidations were considerably different from those of starting polyethylene. For example, the M_w and M_n values of the functionalized LDPE material formed by the nickel-catalyzed oxidation ($M_w = 84.4$ kg/mol, $M_n = 10.2$ kg/mol) were indistinguishable from those of the starting polymer ($M_w = 88.1$ kg/mol, $M_n = 10.2$ kg/mol), whereas the M_w and M_n values of the material formed by the uncatalyzed oxidation process ($M_w = 15.3$ kg/mol, $M_n = 4.8$ kg/mol) were 80% and 50% lower, respectively, than those of the starting LDPE ($M_w = 88.1$ kg/mol, $M_n = 10.2$ kg/mol). These lower values of M_w and M_n indicate that chain cleavage occurred during the oxidation in the absence of the nickel catalyst (see Figure 1). Likewise, the M_w and M_n values for the

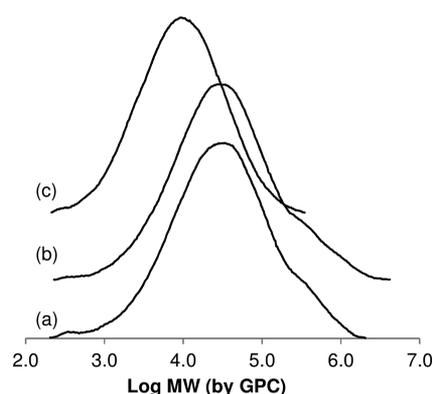


Figure 1. High temperature GPC of (a) LDPE and (b) LDPE oxidized by ^mCPBA catalyzed by Ni catalyst 7 (Table 3, entry 3) and (c) LDPE oxidized by ^mCPBA in the absence of the Ni catalyst (Table 3, entry 4).

polymer produced by the nickel-catalyzed oxidation of the HDPE and LLDPE polymers were nearly identical to those of the starting materials. However, the M_w values of the oxidized HDPE and LLDPE produced with ^mCPBA in the absence of Ni catalyst were 60% and 80% lower and the M_n values were 20% and 60% lower than those values for the respective starting polymer.

We also tested tris(pyridylmethyl)amine-ligated catalyst 8 for the oxidation reactions of LDPE (Table 3, entry 5) to test if the differences in selectivities with the different nickel catalysts observed with the smaller alkanes translated to the polyethylenes. The reactions of LDPE catalyzed by this complex generated a product containing only 2.9 functionalities per 100 ethylene units of the polymer backbone, and the alcohol represented only 58% of the total amount of introduced functionalities. Moreover, the materials obtained from the reaction catalyzed by 8 contained 20% of ester functionality, and the GPC analysis of this material indicated that chain cleavage occurred. The molecular weight of the material resulting from the oxidation of LDPE in the presence of catalyst 8 was 20–30% lower than that of the starting polymer.

Properties of the Functionalized Polyethylenes. To determine the effect of the functionalization on the basic properties of the polymers, we measured the melting temperatures and the wetting properties. The melting temperatures of the starting and functionalized polyethylenes are

shown in Table 3. The T_m values of the LDPE, HDPE, and LLDPE generated by the catalyzed oxidations with m CPBA are similar to those of the unfunctionalized polymers. This result is in accordance with the results on hydroxyl-containing branched polyethylenes obtained from saponification and radical copolymerization in which the melting temperature (111.2 °C) and crystallinity were not substantially affected by the presence of 0.48–6.6 hydroxyl groups per 100 monomer units (105.4 °C < T_m < 116.5 °C)⁵⁰ and on linear polyethylenes containing various amounts of hydroxyl groups obtained from acyclic diene metathesis (ADMET) polymerization and hydrogenation (120 °C < T_m < 128 °C).⁵¹ However, the melting temperatures of materials we prepared from uncatalyzed oxidation of LDPE were lower than that of the parent polymer (96.0 vs 108.8 °C) because the molecular weight of this oxidized material is lower than that of the starting LDPE ($M_n = 4.8$ kg/mol vs $M_n = 10.1$ kg/mol).⁵²

The static water contact angles of functionalized LDPE, HDPE, and LLDPE and the respective parent polymers were measured by the sessile drop method (see Figure S11). The measured water contact angles of starting LDPE, HDPE, and LLDPE were found to be 96.7°, 90.2°, and 91.5° respectively. The contact angles of LDPE, HDPE, and LLDPE obtained from Ni-catalyzed functionalization process (Table 3, entries 7, 10, and 12) were lower: 84.9°, 82.9°, and 88.1° respectively. These lower values are, presumably, due to the introduction of polar functionality into the materials.

Synthesis and Blending of Graft Copolymers from Hydroxy-Polyethylene. Hydroxyl groups on polyolefins have been proposed to be sites for attaching larger polar groups or grafting copolymers.^{27,53–56} Block and graft copolymers based on polyesters are of particular interest due to their biodegradability and biocompatibility;⁵⁷ they have been employed in various biomedical applications⁵⁸ and in the compatibilization of biodegradable polymer blends.^{59–62}

As one demonstration of the potential of the hydroxyl groups in our functionalized polyethylenes to be reactive sites, we used them as macroinitiators for the polymerization of ϵ -CL to obtain polyethylene-graft-poly(ϵ -caprolactone) (PE-g-PCL) possessing microstructures distinct from those prepared previously. Prior studies on the synthesis of poly(vinyl alcohol)-graft-poly(ϵ -caprolactone) (PVA-g-PCL) and poly(ethylene-co-vinyl alcohol)-graft-poly(ϵ -caprolactone) (EVOH-g-PCL) by ring-opening polymerization of ϵ -caprolactone resulted in formation of short PCL arms with low degrees of polymerization (DP = 4–29), and the reported grafts contained unreacted hydroxyl and acetoxy groups.^{60,63} Recently, hydroxylated HDPE obtained via ring-opening metathesis copolymerization of cyclooctene and 5-hydroxycyclooctene was used as macroinitiator for the grafting of PCL.⁵³

For our synthesis of polyethylene-graft-poly(ϵ -caprolactone) materials, we used the hydroxylated low-density polyethylene (LDPE-OH) and the hydroxylated high-density polyethylene (HDPE-OH) obtained from the reaction with m CPBA in the presence of $[\text{Ni}(\text{Me}_4\text{Phen})_3](\text{BPh}_4)_2$. We conducted the grafting of ϵ -CL by ring-opening of the lactone with tin(II) 2-ethylhexanoate as catalyst in DCE at 100 °C for 40 h with the ratio of $[\text{Sn}]_0:[\text{OH}]_0 = 0.1:1$. The length of the PCL arm was controlled by the ratio of the hydroxyl groups on the backbone of the polyethylene to ϵ -CL, and was varied between 30 and 100.^{64,65} Consistent with this ratio of hydroxyl group to ϵ -CL,

the degree of polymerization of the grafts on the PE-g-PCL we obtained ranged from 29.1 to 95.3 (Table S10, entries 1–3).

The purity and composition of the obtained PE-g-PCL graft copolymers were assessed by ¹H NMR spectroscopy (see Figure S6). The ¹H NMR spectrum of the graft copolymer LDPE-g-PCL in CDCl₃ lacked the resonance corresponding to the hydrogen located alpha to the hydroxyl group ($\text{CH}_\alpha\text{-OH}$, 3.63 ppm, TCE-*d*₂) of the oxidized low-density polyethylene (LDPE-OH). Instead, it contained a resonance at 4.86 ppm, corresponding to the secondary alpha hydrogen of the esterified hydroxyl group ($\text{CH}_\alpha\text{-OC(O)-}$). The presence of this new resonance and the characteristic peaks of polycaprolactone at 4.07 ppm ($\text{CH}_{2\epsilon}\text{-OC(O)-}$), 3.66 ppm ($\text{CH}_{2\epsilon}\text{-OH}$), and 2.32 ppm ($\text{OC(O)-CH}_{2\alpha}\text{-}$) provide strong evidence that the ϵ -CL was grafted to the hydroxylated low-density polyethylene.

The molecular weight and thermal properties of polymers assessed by GPC and DSC were consistent with a grafted material. As expected for grafting by a living polymerization of caprolactone,^{66,67} the PDI of the PE-g-PCL material was narrower than that of the starting polymer. For instance, the M_n of the graft copolymer with the degree of polymerization of PCL arms equal to 29.1 was 62% higher than that of the starting hydroxylated low-density polyethylene, and the PDI of the graft was 24% lower than that of the hydroxylated polymer (entry 1, Table S10). Consistent with microphase separation of two immiscible materials, we observed two melting temperatures.^{60,63} The first T_{m1} was near 60 °C and corresponds to the PCL segments, while the second melting temperature was near 110 °C and corresponds to the low-density polyethylene. The T_{m1} values were higher for the polymers containing longer PCL arms (entries 1–3, Table S10), whereas the values of T_{m2} corresponding to the low-density polyethylene phase were lower for polymers containing longer PCL arms, due to disruption of the crystallization of the polyethylene by the polycaprolactone. The DSC analysis also revealed one glass transition temperature (T_g) near –60 °C, which is typical of the PCL segments. The T_g values for polyolefins are typically below the lowest –80 °C temperature accessible by the instrumentation.

Blending of two polymers can generate new materials with valuable properties from commercially available polymers,⁶⁸ and graft copolymers have been used as compatibilizer for binary, immiscible blends.^{59–62} Indeed, the synthesized PE-g-PCL graft copolymer (1.8 PCL arms/100 ethylene monomers, DP of PCL = 95.3, $M_n = 43.7$ kg/mol, PDI = 6.09) compatibilized binary blends of PCL (Aldrich, $M_n = 10.0$ kg/mol, PDI = 1.40) and LDPE (Aldrich, $M_n = 10.2$ kg/mol, PDI = 8.65). Two blends were prepared, one a mix of LDPE and PCL in an 80:20 ratio without the PE-g-PCL graft copolymer and a second with the same composition containing 10 wt % of PE-g-PCL. Scanning electron micrographs of the LDPE/PCL (80:20 wt %) blend without graft copolymer showed that the material contains two immiscible phases, consisting of spherical PCL particles dispersed in LDPE, reflecting the well-known, poor interfacial adhesion between the two materials (Figure S10a).⁶⁹ In contrast the LDPE/PCL (80:20 wt %) blend compatibilized with 10 wt % PE-g-PCL resulted in a material containing small, distorted spherulites and nearly indistinguishable phases (Figure S10c). These data show that a material derived from hydroxylation of commercial polyethylene can serve a practical function, such as compatibilizing blends of polyethylenes and polar materials.

CONCLUSION

The nickel complex $[\text{Ni}(\text{Me}_4\text{Phen})_3](\text{BPh}_4)_2$ in which Me_4Phen is 3,4,7,8-tetramethyl phenanthroline catalyzes the hydroxylation of alkanes with high turnovers without cleavage of the C–C bonds of linear alkanes. The oxidation of cyclohexane catalyzed by $[\text{Ni}(\text{Me}_4\text{Phen})_3](\text{BPh}_4)_2$ (0.01 mol %), with ${}^m\text{CPBA}$ as oxidant, formed cyclohexanol with a total TON of 5560 and 10.5:1 ratio of alcohol to (ketone + ester). The oxidation of *n*-octadecane occurs with 15.5:1 selectivity for the alcohol over ketone, with only trace amounts of ester. Related reactions in the absence of catalyst gave large amounts of ester functionalities.

This selective, catalytic oxidation was applied to the hydroxylation of polyethylenes with various microstructures (LDPE, HDPE, and LLDPE). The combination of $[\text{Ni}(\text{Me}_4\text{Phen})_3](\text{BPh}_4)_2$ as catalyst and ${}^m\text{CPBA}$ as oxidant led to the introduction of 2.0 to 5.5 functional groups (alcohol, ketone, alkyl chloride) per 100 monomer units with alcohols consisting of up to 88% of the total functionality introduced. In contrast to any other oxidation of polyethylene reported previously, this combination of catalyst and reagent led to the hydroxylation of polyethylenes without significant modification of the molecular weight parameters of the polymers. The M_w values of the functionalized polyethylenes (HDPE, LDPE, LLDPE) formed by the uncatalyzed oxidation were significantly lower than those of parent polymer, indicating that chain cleavage occurred during the oxidation in the absence of the nickel catalyst. The resulting polymers were used as macro-initiators for creating graft copolymers with $\epsilon\text{-CL}$, and the resulting material was used to compatibilize a polar polymer with polyethylene. Applications to adhesion of polymer films and to cross-linking immiscible materials will be part of future studies with these materials.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscentsci.7b00255.

Experimental details, synthetic procedures, and spectral data (PDF)

Crystallographic data for 7 (CIF)

AUTHOR INFORMATION

Corresponding Author

*E-mail: jhartwig@berkeley.edu.

ORCID

Sunwoo Lee: 0000-0001-5079-3860

John F. Hartwig: 0000-0002-4157-468X

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Notes

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