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Regiospecific Side-Chain Functionalization of Linear Low-Density Polyethylene with Polar Groups**

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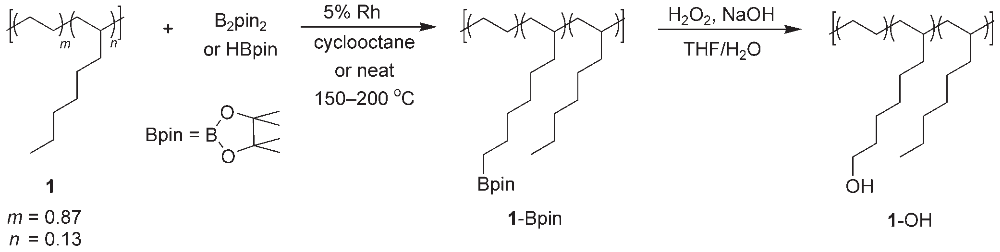
The incorporation of polar functional groups along the backbone of polyolefins can significantly alter the physical properties and increase the utility of these commodity materials.[1,2] A polar functionality can improve the interaction of these materials with other polymers and their adhesion to metals or glass. Moreover, functional groups in a polymer chain can serve as initiation sites for the formation of graft copolymers.[2] Thus, polyolefins with polar groups have been a target for polymer synthesis.[2–4]

We recently reported the synthesis of such materials by conducting selective, catalytic functionalization of the pendant methyl groups of a model atactic amorphous polybutene of moderate molecular weight[5] and of commercial polypropylenes of various tacticities.[6] Both polybutene and polypropylene contain an abundance of accessible methyl groups. In contrast, commercially important linear low-density polyethylenes (LLDPEs), generated from ethylene and an alpha-olefin, such as octene, contain a small population of methyl groups. Because the yields of the borylation of aliphatic C–H bonds depend on the population of methyl groups in the system,[7] the extension of the functionalization of polybutene and polypropylene to the functionalization of amorphous polybutene to LLDPE is challenging. Moreover, these polyolefins have been converted into materials with boronic esters and alcohols, but not into materials with groups such as amines or carbonyls which would be useful for generating ionic polymers or graft copolymers. We have recently met these challenges. Herein, we report the regiospecific functionalization of an ethylene–octene copolymer using pinacolborane (HBpin) or bis(pinacolato)diboron (B_2pin_2) as reagent in the presence of a rhodium catalyst, and the conversion of the resulting borylated polymer into a family of materials with hydroxy, amino, and formyl groups at the termini of the hexyl side chains.

As with the borylation of small alkanes,[8] the rhodium-catalyzed reactions of HBpin and B_2pin_2 at 150–200 °C with a copolymer **1** of ethylene (87 mol %) and 1-octene (13 mol %) which has a number-average molecular weight (M_n) of 112 kg mol^{-1} and a polydispersity index (PDI $= M_w/M_n$) of 1.9,[9] produced the corresponding polymer with boryl groups at the termini of the side chains. The isolated **1**-Bpin was then oxidized with NaOH/hydrogen peroxide in a mixture of THF and H_2O to give the corresponding polymer **1**-OH with hydroxy groups at the termini of the side chains (Scheme 1).

Both **1**-Bpin and **1**-OH were characterized by NMR spectroscopy. The borylated material **1**-Bpin gave rise to a broad peak in the ^{11}B NMR spectrum at $\delta = 34$ ppm for the alkyl–Bpin moiety and a resonance in the ^{1}H NMR spectrum at $\delta = 0.75$ ppm for the methylene groups adjacent to the Bpin units. The ^{13}C NMR spectrum contained two signals of low intensity at $\delta = 24.9$ and 82.8 ppm from the Bpin groups. DEPT ^{13}C NMR spectroscopy confirmed that these signals corresponded to methyl and quaternary carbon atoms.



Scheme 1. Regiospecific functionalization and subsequent oxidation of linear low-density polyethylene (LLDPE).

After treatment of **1**-Bpin with basic hydrogen peroxide, no signals for an alkyl–Bpin moiety were observed in the ^{1}H and ^{13}C NMR spectra, consistent with complete conversion of **1**-Bpin into the hydroxylated material **1**-OH. The ^{1}H NMR spectrum contained a triplet at $\delta = 3.64$ ppm, and the ^{13}C NMR spectrum contained a singlet at $\delta = 63.2$ ppm for the methylene group that lies alpha to the hydroxy group. An attached proton test confirmed the assignment of the signal at $\delta = 63.2$ ppm as a methylene resonance. The relative intensities of the ^{1}H NMR signals of the hydroxymethyl methylene protons and of the unfunctionalized methyl groups of the side

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chains were used to calculate the fraction of side chains that were functionalized with hydroxy groups (Table 1 and Table 2).

Data on the molecular weight and degree of functionalization of polymers generated from **1** are summarized in Table 1 (HBpin) and Table 2 (B_2pin_2). Size-exclusion chromatography (SEC) data show that the borylation and hydroxylation processes do not lead to a significant change in the molecular weight or polydispersity of the parent polymer **1**. Thus, the rhodium-catalyzed reaction and subsequent oxidation led to the addition of a polar functionality without causing significant chain scission or coupling between polymer chains as typically observed in the free-radical modification of polyolefins.[10,11]

We defined the efficiency of the functionalization reaction as the ratio of hydroxy groups in the polymer to the boron reagent added initially. As complete conversion of **1**-Bpin into **1**-OH is supported by the disappearance of resonances for alkyl–Bpin in the NMR spectra, we assume that the reported OH efficiency is also representative of the initial efficiency of the addition of Bpin. Reactions of **1** with HBpin in the presence of [Cp*Rh(η^4-C_6Me_6)] and [Cp*Rh(C_2H_4)$_2$] (Cp* = pentamethylcyclopentadiene) occurred with similar efficiencies, whereas reactions with [Cp*RhCl_2]$_2$ led to incorporation of less boron into the polymer (Table 1, entries 1–3). Reactions of B_2pin_2 catalyzed by [Cp*Rh(η^4-C_6Me_6)] led to **1**-Bpin with a higher concentration of boryl groups in the polymer than reactions catalyzed by [Cp*RhCl_2]$_2$ or [Cp*Rh(C_2H_4)$_2$] under otherwise identical conditions (Table 2, entries 1–3) and showed more effective functionalization than those with HBpin as the boron reagent. Therefore, the combination of B_2pin_2 reagent and [Cp*Rh(η^4-C_6Me_6)] catalyst was chosen to study the effects of solvent, temperature, and the ratio of boron to hexyl side chains (Table 2, entries 3–11). Reactions performed at 150 °C in cyclooctane generated a polymer with the highest concentration of functionalized hexyl side chains, which could be controlled by varying the ratio of B_2pin_2 to side chain without adversely affecting the molecular parameters under the optimized conditions (Table 2, entries 3, 5, 7, and 10). For example, the degree of functionalization increased by a factor of two when the ratio of B_2pin_2 to hexyl groups was increased from 0.3 to 0.7, but a further increase in the ratio of diboron reagent to hexyl groups from 0.7 to 1.0 did not increase the percentage of functionalized side chains. The maximum percentage of side chains that we were able to functionalize with hydroxy groups was about 20 % (Table 2, entries 7 and 10).

We also explored the conversion of the selectively hydroxylated LLDPE into materials with other types of polar functionality. At this time, no method to directly convert an alkyl pinacolboronate into an alkylamine or aldehyde is known. Thus, we developed conditions to convert

Table 1: Molecular weight and degree of functionalization of LLDPE after selective modification with pinacolborane (HBpin).[a]

Entry	Ratio[b]	Rh catalyst	T [°C]	**1**-Bpin		**1**-OH		OH [mol %][d]	Efficiency [%][e]
				M_n [kg mol^{-1}][c]	PDI[c]	M_n [kg mol^{-1}][c]	PDI[c]		
1	0.2	[Cp*RhCl_2]$_2$	165	109	2.1	110	1.8	0.8	4
2	0.2	[Cp*Rh(C_2H_4)$_2$]	165	87.9	1.8	115	1.9	2.5	13
3	0.2	[Cp*Rh(η^4-C_6Me_6)]	165	110	1.9	103	1.6	2.5	13
4	0.5	[Cp*Rh(η^4-C_6Me_6)]	150	87.0	1.6	101	1.9	3.6	7
5	1.0	[Cp*Rh(C_2H_4)$_2$]	150	–	–	96.0	2.0	5.6	6
6	2.0	[Cp*Rh(η^4-C_6Me_6)]	150	98.2	1.8	108	1.7	2.4	1

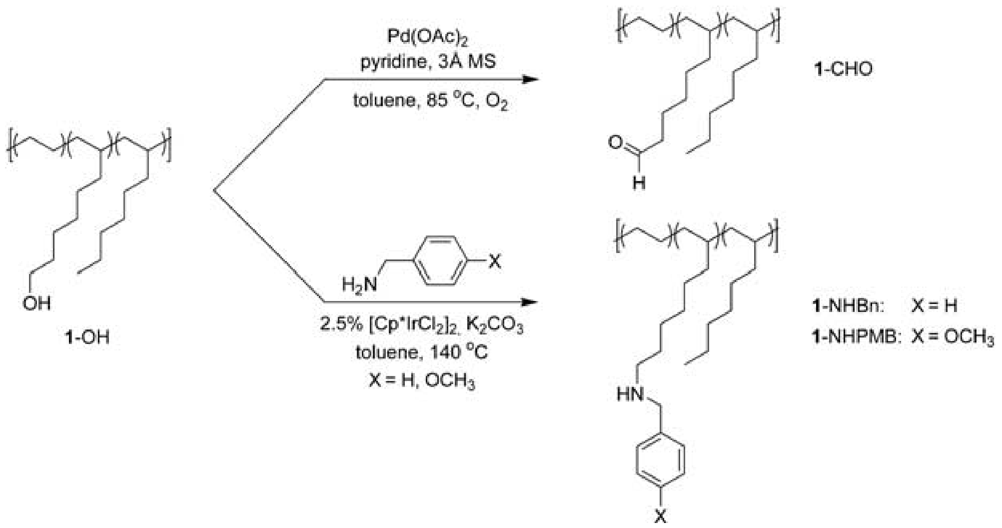
[a] Borylations were conducted on 150 mg of polymer with 5 mol % of Rh relative to HBpin in a sealed tube for 36 h. [b] Ratio of HBpin to hexyl side chains. [c] Measured by size-exclusion chromatography relative to polystyrene standards (THF as eluent at 40 °C); values for unfunctionalized LLDPE (**1**): M_n = 112 kg mol^{-1}; PDI = 1.9.[9] [d] Ratio of -CH_2OH to -CH_3 groups in the functionalized polymer (×100). [e] Molar ratio of hydroxy groups in the polymer to boron reagent added.

Table 2: Molecular weight and degree of functionalization of LLDPE after selective modification with bis(pinacolato)diboron (B_2pin_2).[a]

Entry	Ratio[b]	Rh catalyst	T [°C]	**1**-Bpin		**1**-OH		OH [mol %][d]	Efficiency [%][e]
				M_n [kg mol^{-1}][c]	PDI[c]	M_n [kg mol^{-1}][c]	PDI[c]		
1	0.2	[Cp*RhCl_2]$_2$	165	98.2	2.0	102	2.4	3.6	18
2	0.2	[Cp*Rh(C_2H_4)$_2$]	165	92.7	2.1	121	2.1	4.9	25
3	0.2	[Cp*Rh(η^4-C_6Me_6)]	165	97.6	2.1	114	2.1	6.8	34
4[f]	0.3	[Cp*Rh(η^4-C_6Me_6)]	200	–	–	–	–	5.4	18
5	0.3	[Cp*Rh(η^4-C_6Me_6)]	150	101	2.1	102	2.1	10.0	33
6[f]	0.3	[Cp*Rh(η^4-C_6Me_6)]	150	–	–	–	–	5.9	20
7	0.7	[Cp*Rh(η^4-C_6Me_6)]	150	–	–	–	–	19.0	27
8	1.0	[Cp*Rh(η^4-C_6Me_6)]	200	95.6	1.9	101	1.9	14.4	14
9[f]	1.0	[Cp*Rh(η^4-C_6Me_6)]	200	83.1	1.7	85.2	1.9	12.0	12
10	1.0	[Cp*Rh(η^4-C_6Me_6)]	150	96.5	2.0	94.1	2.1	19.2	19
11[f]	1.0	[Cp*Rh(η^4-C_6Me_6)]	150	107	1.8	102	1.9	15.5	16

[a] Borylations were conducted on 150 mg to 5 g of polymer with 5 mol % of Rh relative to B_2pin_2 in neat polymer or in cyclooctane under nitrogen for 36 h. [b] Ratio of B_2pin_2 to hexyl side chains. [c] Measured by size-exclusion chromatography relative to polystyrene standards (THF as eluent at 40 °C); values for unfunctionalized LLDPE (**1**): M_n = 112 kg mol^{-1}; PDI = 1.9.[9] [d] Ratio of CH_2OH to CH_3 groups in the functionalized polymer (×100). [e] Molar ratio of hydroxy groups in the polymer to diboron reagent added. [f] No solvent.

the hydroxylated polymers into materials with formyl and amino groups. Although several reactions of stoichiometric reagents are available for the oxidation of alcohols to aldehydes, we chose the catalytic route with water as the only byproduct as shown in Scheme 2. The conversion of **1**-OH (Table 2, entry 5) into the aldehyde-containing polymer **1**-CHO proceeded with molecular oxygen in the presence of $Pd(OAc)_2$ under the mild conditions reported for low-molecular-weight alcohols by Nishimura et al.[12] and without adversely affecting the molecular parameters (Table 3). As with the hydroxy groups of **1**-OH, the aldehyde groups in **1**-CHO were easily identified by NMR spectroscopy. Resonances for a formyl hydrogen center and a methylene group alpha to an aldehyde were observed as a singlet at $\delta = 9.77$ ppm and a triplet at $\delta = 2.42$ ppm in the ^{1}H NMR spectrum and as resonances at $\delta = 202.4$ and 44.0 ppm, respectively, in the ^{13}C NMR spectrum. The formyl group was also detected by the C=O stretching band at $\tilde{\nu} = 1711\ \text{cm}^{-1}$ in the IR spectrum.



Scheme 2. Conversion of **1**-OH to formyl- (**1**-CHO) and amino-functionalized (**1**-NHBn, **1**-NHPMB) LLDPEs.

Table 3: Molecular weight data for formyl- and amino-functionalized LLDPEs.

Entry	M_n [kg mol^{-1}][a]	PDI
1-OH	102	2.1
1-CHO	105	1.8
1-NHBn[b]	67.0	2.1
1-NHPMB[b]	49.9	2.1

[a] Measured by SEC relative to polystyrene standards (THF as eluent at 40 °C). [b] M_n and PDI measured from an initial solution of polymer in toluene, eluted with THF at 40 °C.[13]

We converted the hydroxylated polymers into amino-substituted polymers by an iridium-catalyzed amination of alcohols.[13] The reaction of polymer **1**-OH with benzylamine ($BnNH_2$) and *p*-methoxybenzylamine ($PMBNH_2$) in toluene at 140 °C for 48 h in the presence of 2.5 mol % of $[Cp^*IrCl_2]_2$, relative to the hydroxy groups, and K_2CO_3 as the base (Scheme 2) formed a polymer with benzylamino and *p*-methoxybenzylamino groups in place of hydroxy groups at the termini of the functionalized side chains. The ^{1}H and ^{13}C NMR spectra of the product polymers **1**-NHBn and **1**-NHPMB showed an absence of resonances from a methylene group alpha to the oxygen atom. The ^{1}H NMR spectrum of **1**-NHBn contained new singlet and triplet methylene resonances at $\delta = 3.79$ and 2.62 ppm, and the ^{13}C NMR spectrum contained two new resonances at $\delta = 54.1$ and 49.6 ppm for the methylene units of the benzyl group and the methylene unit of the side chain alpha to the nitrogen center. ^{1}H and ^{13}C NMR data for **1**-NHPMB were similar but displayed a ^{1}H NMR resonance at $\delta = 3.77$ ppm and a ^{13}C NMR resonance at $\delta = 55.4$ ppm for the methoxy groups.

Molecular-weight data from SEC of these amino-substituted polymers are included in Table 3. The PDI values and peak shapes of **1**-NHBn and **1**-NHPMB are similar to those of **1**-OH, suggesting that chain scission and chain coupling have not occurred. However, the average molecular weights of the **1**-NHR polymers relative to polystyrene standards are significantly lower than those of the starting hydroxylated polymer **1**-OH. We presume that the M_n values of the amine-functionalized polymers are lower owing to a combination of changes in the solubility[14] and the hydrodynamic volume of the polymer from the addition of the amino groups, and that unfunctionalized polystyrene standards do not provide an appropriate representation of the molecular weight of the material with basic groups.

In summary, we have demonstrated that functionalization of a commercial linear low-density polyethylene can be accomplished through the rhodium-catalyzed borylation of alkanes and subsequent oxidation without significantly altering the molecular weight of the starting polymer. Moreover, the hydroxy groups can be further modified to generate polymers with formyl and amino groups at the termini of the side chains.

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[9] Because **1** was significantly less soluble in THF than the functionalized polymers, a solution of **1** in toluene was injected into the SEC system with THF as the eluent.

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