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Rhodium-Catalyzed, Regiospecific Functionalization of Polyolefins in the Melt

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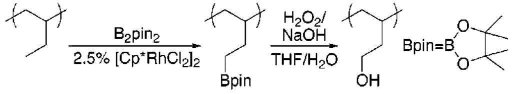
The activation of alkane C−H bonds with transition metals has a long history.[1] Homogeneous oxidative addition of alkane C−H bonds was one of the most significant milestones[2,3] and suggested that regioselective alkane functionalization should be possible. Most research has targeted the conversion of methane to liquid fuel stocks, but this goal does not exploit the potential regioselectivity of homogeneous catalytic C−H activation.[4] While regiospecific oxidative additions have been observed,[5−7] only modest progress on catalytic, regiospecific functionalization had been achieved until recently.[8,9]

In the past year, linear alkanes were converted regiospecifically to terminal alkylboranes using a rhodium catalyst under thermal conditions.[8] This development created the opportunity to address an alternative application of alkane functionalization: the regiospecific modification of polyolefins. Incorporation of polar functionality along the backbone[10−12] or on branches[13] of these commercially useful macromolecules would lead to materials that display enhanced properties (e.g., adhesive and barrier[14]), that would be useful as blend compatibilizers,[15] and that could be used as macroinitiators to prepare graft copolymers.[16,17] A selective functionalization of commodity polyolefins would bypass the challenge of developing highly active polymerization catalysts that both tolerate and incorporate functionalized comonomers.[10,11,18] We show that the rhodium-catalyzed alkane borylation, in conjunction with simple oxidation of the alkylboronate esters to alcohols (Scheme 1),[19] effectively forms polyolefins with hydroxyl groups at the terminal positions of branches. This chemistry constitutes a rare example of preparative, selective alkane functionalization.

We used as a model polyolefin for this study polyethylethylene (PEE). This material was prepared using a two-step process involving an anionic polymerization of butadiene, which occurred by roughly 86−99% 1,2 additions, followed by hydrogenation of the polydiene.[20,21] The final material contained between 40 and 50 ethyl branches per 100 backbone carbons after hydrogenation. Treatment with sulfuric acid and alumina removed the few unreacted olefin units, as described previously for shorter alkanes.[22] The narrow molecular weight distribution of these materials allowed for the easy identification of chain scission or cross-linking that often plague nonselective polyolefin modifications.[23−25] Our studies focused on two materials: a low-molecular-weight polymer (PEE-1, $M_n = 1.2$ kg/mol, PDI = 1.11), which allowed for detailed molecular characterization by mass spectrometry, and a high-molecular-weight material (PEE-2, $M_n = 37$ kg/mol, PDI = 1.06), which more closely resembles a commercial polymer and allows for evaluation of the physical properties of the functionalized polymer.

The polymer functionalizations were conducted with 5 mol % $[Cp^*RhCl_2]_2$[26,27] and various ratios of diboron reagent to polymer for 12 h, after which time the boron reagent was fully consumed.

Scheme 1. Catalytic Modification of PEE



In most C−H activation processes, the alkane is present in excess quantities or as solvent. Thus, we conducted reactions in neat polymer substrate, which are fluid at the reaction temperatures (150−200 °C).[28] With this procedure, the polymer chains are less abundant than the boron reagent, but the polymer side chains are equal or greater in abundance. The products were isolated as the boronate ester derivative or were treated with basic hydrogen peroxide in a mixture of THF and H_2O to oxidize the boronate ester groups to the corresponding alcohols.[19]

In one set of experiments, we allowed PEE-1 to react at 150 °C for 36 h with bis-pinacoldiboron (B_2pin_2) in a 0.25:1 ratio of borane to chains of PEE-1 (B_2pin_2/monomer = 0.012). This procedure provided the borylated product, as indicated by a ^{11}B NMR resonance at δ35 that corresponds to alkylBpin groups. In addition, field desorption mass spectrometry (FD-MS) data showed a clear conversion of unfunctionalized polymer to the corresponding borylated material (Figures S1 and S2, Supporting Information). The functionalized material was separated from the unfunctionalized material using standard silica gel chromatography with hexane and ethylacetate as eluent. After oxidation of the functionalized polymer, material that contained, almost exclusively, one hydroxyl group per main chain was observed by NMR spectrometry and FD-MS.

We conducted the same reaction using PEE-1 and a ratio of B_2pin_2 to polymer chain of 4 (B_2pin_2/monomer = 0.2) on a gram scale to generate samples that were more highly functionalized. We isolated 70% yield of functionalized polymer based on polymer weight after oxidation. A combination of ^1H NMR, ^{13}C NMR, and IR spectroscopies (Figure 1) revealed the degree and type of functionalization. The methylene protons α to the hydroxyl group of the functionalized material resonated at 3.7 ppm, and the carbon α to the same group resonated at 60.15 ppm. The assignment of these signals as methylene resonances was confirmed by observing inversion of the resonance at δ 60.15 in the 135° DEPT ^{13}C NMR spectrum. No signals corresponding to a methine group α to oxygen were observed. The IR spectrum of the material showed an absorption band at 3300 cm^{-1} for the O−H stretch. All of these data are consistent with the regioselective functionalization of pendant CH_3 groups in the polymer chain, as depicted in Scheme 1.

Additional characterization of this hydroxylated product was conducted by matrix-assisted laser desorption/ionization mass spectrometry (MALDI-MS). The MALDI-MS spectrum exhibited peaks between 850 and 2000 *m/z*; the data between 1340 and 1460 *m/z* are shown in Figure 2. Each envelope of peaks was assigned to isotopomers of the same molecular species containing only C,

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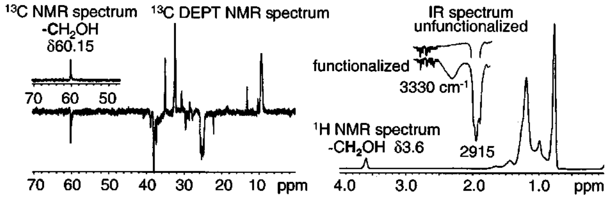

Figure 1. (Left) δ 50−70 ppm region of the ^{13}C NMR and 135° ^{13}C DEPT NMR spectrum of PEE-1 after catalytic borylation and oxidation. (Right) ^{1}H NMR spectrum of the same sample and IR (inset) of the CH and OH stretching region of the starting and hydroxylated polymer.

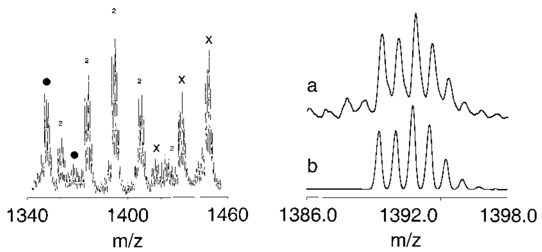

Figure 2. (Left) MALDI-MS of a hydroxylated PEE with 2.6 hydroxyl groups per chain on average. ●, $C_{84}H_{170}O_nAg$ series (n = 1, 2); △, $C_{88}H_{178}O_nAg$ series (n = 1−5); and ×, $C_{92}H_{186}O_nAg$ series (n = 1, 2). (Right) (a) an expanded version of the $C_{88}H_{178}O_3Ag$ peaks and (b) the theoretical pattern based on natural abundance isotopes. The two small peaks at m/z 1388 and 1389 may be due to elimination of H_2O from a $C_{88}H_{178}O_4$ species under the analysis conditions.

Table 1. Molecular and Physical Properties of Modified PEE-2 (M_n = 37 kg/mol, PDI = 1.06, T_g = − 42 °C)

		borylated polymer			hydroxylated polymer				
entry	ratio[a]	M_n[b]	PDI	T_g[c]	M_n[b]	PDI	T_g[c]	wt % −OH[d]	yield (%)[e]
1	0.07	39.6	1.16	−36	38.9	1.28	−20	1.5	93
2	0.3	52.0	1.09	−38	40.1	1.30	−2	3.1	45
3	1	43.7	1.49	−31	32.9	2.12	11	4.4	20

[a] Initial ratio of B_2pin_2:monomer. Values for unfunctionalized material: M_w = 49.1 kg/mol, PDI =1.03, and T_g = −42 °C. [b] Number-average molecular weight reported in kg/mol. [c] Glass transition temperature reported in °C. We estimate the error in these values at ±5 °C. [d] Fully functionalized PEE would contain about 23 wt % −OH. [e] The ratio of wt % hydroxyl groups to maximum wt % calculated from the ratio of diboron reagent to monomer.

H, O, and 1 Ag (silver triflate was used as cationizing agent). The molecular formulas are consistent with polymeric products containing from 1 to 5 hydroxyl groups. Around the center of the molecular weight distribution, material corresponding to chains with 3 hydroxyl groups generated the largest peak within each envelope of peaks for material with the same chain length. These data were consistent with the average number of 2.6 hydroxyl groups per chain determined by ^{1}H NMR spectroscopy. In Figure 2, the spectrum corresponding to the species with 22 monomer units and two hydroxyl groups ($C_{88}H_{178}O_3Ag$) is shown. The accompanying pattern calculated from the natural abundance isotopic distribution further corroborates our assignment. Analysis of the signals between 850 and 2000 m/z gave a number-average molecular weight (M_n) of 1.34 kg/mol and a PDI of 1.05. The PDI of this product, as determined by SEC, was also 1.05. Thus, the functionalization created little or no disruption of the polymer molecular weight distribution.

Functionalization of higher molecular weight PEE-2 was performed at various ratios of diboron reagent to monomer unit (Table 1). Reactions were conducted at 150 °C, and the product was oxidized with basic hydrogen peroxide in a THF/H_2O solvent mixture. For ease of separation from the pinacol byproduct on a small scale, the polymer was passed through lipophilic Cephadex. The ^{1}H and ^{13}C NMR spectra, which contained signals for methylene groups α to oxygen and lacked signals for quaternary or methine positions with hydroxyl groups attached, were again consistent with a regioselective conversion of methyl groups on the polymer side chains to hydroxymethyl groups. The borylated materials usually exhibited molecular weight data similar to those of the starting polyolefin. However, the samples with a large number of boryl groups showed some coupling of chains during the formation of hydroxylated sample that increased the PDI. The level of −OH incorporation generally increased with increasing ratios of B_2pin_2 to polymer.

To demonstrate the ability of this process to generate materials with altered properties, we measured the change in glass transition temperature for polymer samples that had been treated with varying amounts of diboron reagent and oxidized to the hydroxylated material. An increase in T_g was observed with an increase in the degree of functionalization. For the highest level of −OH incorporation the T_g increased nearly 55 °C, presumably due to enhanced intermolecular interactions through the pendant −OH groups.[29] We observed a monotonic increase in T_g with increasing numbers of −OH groups (Figure S5, Supporting Information).

In summary, we have demonstrated the feasibility of a new approach to generate functionalized polyolefins. The polymers we used in this study are models for the ubiquitous materials based on ethylene or α-olefins as the monomer feed. Future studies will focus on generating alternative functionality from the boryl group and on functionalization of polyolefins formed from different monomers and possessing varied microstructure.

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Supporting Information Available: Reaction procedures, and spectroscopic data for the starting and functionalized polymers (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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