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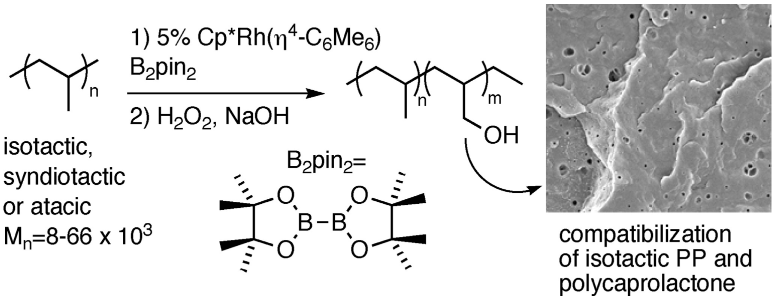

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Catalytic Hydroxylation of Polypropylenes

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Abstract: The regioselective functionalization of both model and commercial polypropylenes of varying tacticity has been conducted by a rhodium-catalyzed functionalization of the methyl C−H bonds of the polymer with diboron reagents. Rhodium-catalyzed borylation of the polypropylenes, followed by oxidation of the boron-containing material, produced polymers containing 0.2−1.5% hydroxymethyl side chains. Both the number-average molecular weights and molecular weight distributions of the polypropylenes were essentially unchanged after the catalytic and oxidative functionalization process. The efficiency of the borylation process was affected by the molecular weight of the polymer, the steric hindrance around the methyl groups, and the ratio of the diboron reagent to the monomer repeat unit. The hydroxylated derivative of the commercial isotactic polypropylene was used as macroinitiator for the aluminum-mediated ring-opening polymerization of ϵ-caprolactone to prepare polypropylene-*graft*-polycaprolactone. This graft copolymer was an effective compatibilizer for melt blends of polypropylene and polycaprolactone.

Introduction

Polyolefins are the most widely used commercial polymers because of their combination of favorable chemical and physical properties, processability, and production from inexpensive feedstocks. Currently, polyolefins constitute nearly 60% of all polymers produced.[1] Although prepared on an enormous scale, the application of these polymeric hydrocarbons is limited by their low surface energies and poor adhesion with more polar materials, metals, and glass.[2,3−5] The effective preparation of polypropylene blends with polar macromolecules often requires the addition of polyolefin block or graft copolymers to prevent macrophase separation.[6−8] Therefore, the synthesis of polyolefins, particularly polypropylene, with polar side chains has been actively pursued.[9−13]

Polypropylene is synthesized using highly electrophilic early transition metal catalysts,[14−20] which are typically poisoned by polar comonomers.[10] While additives such as methylaluminoxane can improve the resistance of the catalyst to deactivation,[21,22] functionalized copolymers can be obtained using traditional catalysts only if the reactivity of the functional group in the monomer is low. Less oxophilic, late transition metal catalysts have been sought to improve the copolymerization of olefins with polar monomers.[23−26] However, these catalysts exhibit modest activity for copolymerization with polar monomers, relative to that observed for the homopolymerization of unfunctionalized olefins. Further, the number-average molecular weight (M_n) of the polymer decreases with increasing incorporation of the polar monomer.[23,25−27] The polymerization of olefins has also been explored in the presence of chain transfer agents, such as a borane,[28] silane,[29] allylbenzene,[30] vinyl chloride,[31] or

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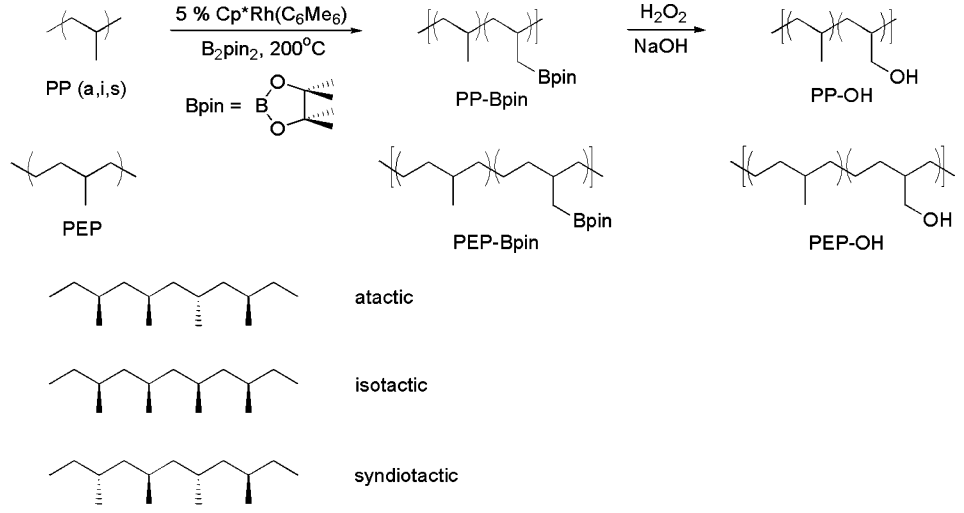
Scheme 1. Regiospecific Functionalization of Poly(ethylene-*alt*-propylene) and Polypropylene



thiophene,[32] to generate materials with functionality in the end group. However, this method is limited because only one functional group is installed into the polymer. The polyethylene and polypropylene derivatives generated with borane-functionalized comonomers and borane reagents as chain transfer agents by Chung and co-workers are the most similar materials to those produced by the chemistry presented here.[28,33−36]

An alternative approach installs polar functionality into polypropylene by chemical modification of the polymer. Current strategies to functionalize polyolefins have relied on highly reactive carbon-based radicals because of the inherently low reactivity of polyolefins.[37] Specifically, the modification of polypropylene has been conducted on an industrial scale by the free-radical grafting of maleic anhydride onto the polymer backbone.[38−40] Unfortunately, the grafting process is accompanied by side reactions, such as β-scission, chain transfer, and coupling reactions, which alter the molecular weight distribution and ultimate properties of the functionalized polymer.[40,41] Significant chain scission compromises mechanical properties, and extensive coupling or cross-linking can render a material impossible to process. Consequently, the development of a methodology for the selective functionalization of commodity polyolefins, which does not alter the molecular weight or polymer architecture, would allow for the preparation of functionalized polyolefins without the need to develop highly active catalysts that both tolerate and incorporate functionalized comonomers.[42]

Efforts toward the modification of polypropylene have had limited success due to the aforementioned competitive side reactions.[42] Moreover, the regiospecific functionalization of polypropylene to produce a material with polar side chains has not been reported. We previously reported an example of the selective functionalization of a model polyolefin, poly(ethylethylene) (PEE),[43] using rhodium-catalyzed functionalization of alkane C−H bonds with borane reagents[44] in the melt. However, extension of this methodology to polypropylene functionalization is not straightforward. First, the borylation is sensitive to steric hindrance. For example, the rhodium-catalyzed borylation of 2-methylheptane occurred preferentially at the less hindered methyl group, and the reaction of methylcyclohexane occurred more slowly and in lower yield than the reaction of a linear alkane.[44] Second, the efficiencies of the borylation of polymer substrates[43] are lower than those of the borylation of linear alkanes,[44] presumably due to the viscosity of the polymer. Thus, the steric hindrance of the methyl groups and the high melt viscosity of polypropylene make the selective borylation of this substrate challenging.

We present our recent success in the regiospecific functionalization of the methyl side chains of a series of polypropylenes, including a model polypropylene copolymer, poly(ethylene-*alt*-propylene) (PEP), a model atactic polypropylene (aPP-1), and a series of commercial polypropylenes with varying tacticities, by the rhodium-catalyzed borylation and subsequent oxidation shown in Scheme 1. This process generates polypropylenes with hydroxyl groups placed exclusively at the termini of the side chains. Further, we report the synthesis of polypropylene-*graft*-polycaprolactone (iPP-*g*-PCL) by ring-opening polymerization of ϵ-caprolactone (CL) from hydroxylated isotactic polypropylene and the use of this graft copolymer to compatabilize blends of immiscible polymers.

Results and Discussion

1. Model Studies with Low-Molecular-Weight Poly(ethylene-*alt*-propylene). We prepared a model low-molecular-weight poly(ethylene-*alt*-propylene) of narrow polydispersity index (PDI) (PEP, $M_n = 8.4$ kg/mol, $M_w/M_n = 1.07$) to investigate the ability of the rhodium-catalyzed chemistry to

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Table 1. Functionalization of Poly(ethylene-*alt*-propylene) (PEP) at 185 °C[a]

			PEP-Bpin			PEP-OH			
entry	Rh catalyst	$[\text{monomer}]_0/[B_2pin_2]_0$[b]	M_n[c]	PDI[d]	yield[e] (%)	M_n[c]	PDI[d]	OH[f] (%)	efficiency[g] (%)
1	$(Cp^*RhCl_2)_2$	20	8.4	1.1	57	8.6	1.1	1.3	26
2	"	10	8.5	1.1	69	8.6	1.1	1.4	14
3	$Cp^*Rh(C_2H_4)_2$	20	8.5	1.2	58	8.4	1.1	1.0	20
4	"	10	8.5	1.1	79	8.5	1.2	1.5	15
5	$Cp^*Rh(\eta^4\text{-}C_6Me_6)$	20	8.5	1.1	70	8.8	1.1	1.4	28
6	"	10	8.6	1.1	78	8.7	1.1	1.7	17

[a] Starting material M_n = 8.4 kg/mol, PDI = 1.1, 5 mol % Rh catalyst loading relative to B_2pin_2. [b] B_2pin_2 = bis(pinacolato)diboron. [c] M_n = number-average molecular weight in kg/mol determined by size exclusion chromatography with THF as eluent. Values are relative to polystyrene standards. [d] PDI = polydispersity index M_w/M_n. [e] Yield of borylated polymer obtained after separation from the unfunctionalized polymer. [f] mol % of CH_2OH relative to methyl side chains. [g] Efficiency of functionalization (the percentage of hydroxyl groups in the final polymer relative to the B_2pin_2 added).

functionalize methyl groups in a material related to polypropylene. The model poly(ethylene-*alt*-propylene) was synthesized by a process that combines anionic polymerization of polyisoprene with catalytic hydrogenation.[45] The narrow PDI of the model polyolefin allows for the identification of side reactions, such as chain coupling or chain cleavage, by using size exclusion chromatography (SEC) to monitor changes in the M_n or PDI of the polymer.

A. Synthesis and Characterization of Borylated and Hydroxylated Poly(ethylene-*alt*-propylene). The borylation of neat PEP with bis(pinacolato)diboron (B_2pin_2) was first conducted under the same conditions that led to the borylation of PEE: 150 °C for 60 h with 2.5 mol % of $(Cp^*RhCl_2)_2$ as catalyst. The borylated PEP (PEP-Bpin) was separated from the unfunctionalized material using column chromatography, as described previously for the functionalization of PEE.[43] Under these conditions, the borylated polymer was obtained in only 10−20% yield based on polymer mass, and the majority of the polymer remained unfunctionalized. Therefore, we studied the borylation of PEP with several rhodium catalysts at higher temperature of 185 °C in efforts to improve the product yields. As shown in Table 1, reactions of the neat polymer at 185 °C in the presence of catalytic amounts of $Cp^*Rh(\eta^4\text{-}C_6Me_6)$ provided 70−80% yield of borylated polymer.

^1H, ^{13}C, and ^{11}B NMR spectroscopy of the borylated polymer obtained after column chromatography clearly showed that the boryl group was installed exclusively at the methyl position of the side chains. The ^1H NMR spectrum contained a new resonance at δ 1.25 corresponding to the methyl groups of the Bpin group. The ^{13}C NMR spectrum exhibited two new chemical shifts of low intensity that were assigned to the methyl carbons and quaternary carbons of the Bpin group at δ 25 and δ 83, respectively. The ^{11}B NMR spectrum contained a broad resonance at δ 34, which is characteristic of an alkyl-Bpin group.

The isolated PEP-Bpin was treated with basic hydrogen peroxide in a mixture of THF and H_2O to oxidize the boronate esters to their corresponding alcohols (Table 1). The hydroxylated polymer was isolated by column chromatography on silica gel. The ^1H NMR spectrum of the isolated hydroxylated PEP (PEP-OH) contained a doublet at δ 3.55 for the methylene protons of the hydroxymethyl group, and the ^{13}C NMR spectrum contained a singlet resonance at δ 66 for the methylene carbon attached to the hydroxyl group. These chemical shifts agree with those for a structurally similar, low-molecular-weight primary alcohol, 2-ethyl-1-butanol.[46] The absence of signals corresponding to secondary [−*C*H(OH)−] or tertiary alcohol [−*C*(OH)(CH_3)−] units is consistent with a selectivity for functionalization of the methyl groups of the polyolefin that mirrors the regiospecific functionalization of low-molecular-weight alkanes.[44]

Integration of the ^1H NMR spectrum of the sample in entry 5 showed that ca. 1.4 mol % of the methyl side chains had been functionalized with a hydroxyl group. With a polymer containing about 70 repeat units, this level of functionality corresponds to approximately 1.7 hydroxyl groups for each of the polymer chains and about 0.6 hydroxyl groups per 100 backbone carbons. The maximum efficiency of the sequence of borylation and oxidation of PEP, defined by the mole ratio of hydroxymethyl groups relative to the initial concentration of B_2pin_2, was 28%.

B. Molecular Weights of the Borylated and Hydroxylated PEP. The molecular weights of the functionalized polymers PEP-Bpin and PEP-OH were determined by SEC. As shown in Table 1, SEC of the functionalized polymers indicated that the sequence of rhodium-catalyzed borylation and oxidation did not significantly alter the M_n or the PDI of the starting material. Only a small amount of coupled byproduct was identified by SEC (Figure 1). Small levels of coupling generally do not negatively affect the performance of materials.[47,48] Most important, no chain scission, which is generally observed during free-radical modification of polypropylene, was observed after the rhodium-catalyzed borylation and subsequent oxidation.

To our knowledge, only one other system leads to functionalization of PEP without chain degradation.[49] This alternative functionalization occurs with a manganese porphyrin complex and a water soluble oxidant in a two-phase process. This methodology introduces tertiary alcohols and ketones into the polymer backbone and does not lead to functionalization of the side chain methyl groups.

2. Regioselective Functionalization of Atactic Polypropylenes. Encouraged by the selective modification of PEP, we conducted the rhodium-catalyzed functionalization of a model atactic polypropylene with a narrow molecular weight distribution (aPP-1, M_n = 44 kg/mol, PDI = 1.2) prepared by anionic polymerization of 2-methyl-1,3-pentadiene, followed by catalytic hydrogenation.[50] For comparison, we also investigated the functionalization of a commercial aPP with a broader molecular weight distribution (aPP-2, M_n = 16 kg/mol, PDI = 2.3).

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Table 2. Functionalization of Polypropylenes at 200 °C

entry	PP[a]	M_n[b]	M_w/M_n	$[\text{monomer}]_0/[B_2pin_2]_0$	PP-Bpin[c]		PP-OH[d]			
					M_n[b]	M_w/M_n	M_n[b]	M_w/M_n	OH[e] (%)	efficiency[f] (%)
1	aPP-1	44.0	1.2	10	46.6	1.3	43.7	1.3	0.70	7.0
2	aPP-1	44.0	1.2	10[h]	48.5	1.2	47.3	1.2	0.79	7.9
3	aPP-2	16.1	2.3	33	15.5	2.5	16.5	2.4	0.68	23
4	aPP-2	16.1	2.3	20	15.8	2.5	16.1	2.5	1.2	24
5	aPP-2	16.1	2.3	10	16.7	2.3	16.3	2.6	1.3	13
6	iPP-1	17.6[g]	2.1	33	15.8[g]	2.1	15.8[g]	2.2	0.76	25
7	iPP-1	17.6[g]	2.1	20	13.9[g]	2.2	17.6[g]	2.1	1.3	26
8	iPP-1	17.6[g]	2.1	10	15.1[g]	2.4	14.4[g]	2.1	1.5	15
9	iPP-2	66.8[g]	3.8	20	58.2[g]	3.0	53.1[g]	2.7	0.27	5.4
10	sPP-1	40.3[g]	2.4	33	37.6[g]	2.4	37.4[g]	2.4	0.22	7.3
11	sPP-1	40.3[g]	2.4	10	34.4[g]	2.3	39.5[g]	2.4	0.35	3.5
12	sPP-2	66.2[g]	3.3	20	54.1[g]	2.7	63.0[g]	3.1	0.31	6.2

[a] aPP = atactic polypropylene; iPP = isotactic polypropylene; sPP = syndiotactic polypropylene. [b] Number-average molecular weight (M_n) measured in THF reported in kg/mol relative to polystyrene standards unless otherwise specified. [c] PP-Bpin = borylated polypropylene. [d] PP-OH = hydroxyl-containing polypropylene. [e] mol % of CH_2OH side chains to unfunctionalized side chains. [f] Efficiency as defined in Table 1. [g] Determined with high-temperature size exclusion chromatography; M_n in units of kg/mol relative to polystyrene standards in 1,2,4-trichlorobenzene. [h] 5 mol % $Cp^*Rh(C_2H_4)_2$ used as catalyst for the borylation step.

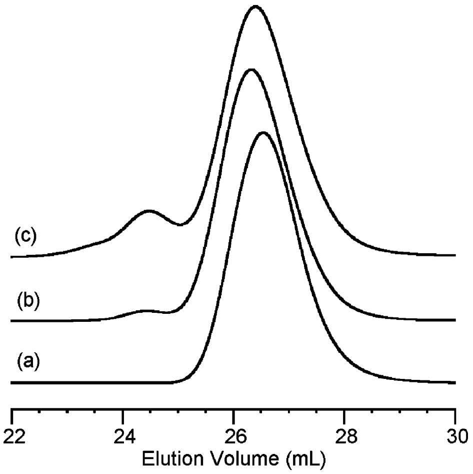

Figure 1. Size exclusion chromatogram (10 mg/mL THF) for (a) PEP [M_n = 8.4, PDI = 1.1], (b) PEP-Bpin [M_n = 8.5, PDI = 1.1], and (c) PEP-OH [M_n = 8.8, PDI = 1.1] (Table 1, entry 5). M_n relative to polystyrene standards. M_n = number-average molecular weight; PDI = polydispersity index; PEP = poly(ethylene-*alt*-propylene); PEP-Bpin = borylated poly(ethylene-*alt*-propylene); PEP-OH = hydroxylated poly(ethylene-*alt*-propylene).

A. Functionalization of a Model Atactic Polypropylene. The rhodium-catalyzed reaction of the model aPP-1 with B_2pin_2 was conducted in the presence of 5 mol % $Cp^*Rh(\eta^4\text{-}C_6Me_6)$ at 200 °C for 24 h. The borylated polymer (aPP-1-Bpin) was isolated in 96% yield based on the mass of the starting aPP-1, after column chromatography. The ^1H NMR spectrum of the borylated material contained a sharp singlet at δ 1.23 that corresponded to the methyl protons of the Bpin group. This signal was not fully resolved, so the degree of borylation could not be determined directly by integration of the ^1H NMR spectrum. The ^{13}C NMR spectrum contained two new resonances at δ 25 and δ 83, corresponding to the methyl and quaternary carbons of the Bpin group, respectively. The ^{11}B NMR spectrum of the borylated product contained a broad resonance near δ 34 for the alkyl-Bpin group.[43]

Oxidation of aPP-1-Bpin with hydrogen peroxide under basic conditions gave the corresponding hydroxyl-containing polypropylene aPP-1-OH in an overall yield of 73% based on the mass of the starting unfunctionalized polymer. The ^1H NMR spectrum of the oxidized product aPP-1-OH contained a new broad resonance at δ 3.51, and the ^{13}C NMR spectrum contained a new resonance at δ 67 corresponding to the hydroxymethyl group. The ^{13}C NMR resonance at δ 67 is consistent with the value calculated from the ^{13}C NMR chemical shifts of 4-hydroxymethyl-2,6-dimethylheptane.[51] Integration of the ^1H NMR spectra of aPP-1-OH showed that 0.70−0.79 mol % of the methyl groups of aPP-1 had been converted to hydroxymethyl groups (Table 2, entries 1 and 2). A value of 0.70 mol % corresponds to three hydroxyl groups per chain or 0.18 hydroxyl groups per 100 backbone carbons.

To gain additional evidence that the functional groups were covalently bound to the polymer, the high-molecular-weight fraction (M_n > ca. 10^4) of a representative sample of aPP-1-OH (Table 2, entry 1) was collected using preparative SEC. ^1H NMR spectroscopy of the high-molecular-weight fraction showed that 0.68 mol % of the monomers contained hydroxymethyl groups, which matches the mol % of functionalized methyl groups in the unfractionated sample in entry 1 of Table 2.

As shown in entries 1 and 2 of Table 2, the M_n and PDI values of both the borylated polymer aPP-1-Bpin and the hydroxylated polymer aPP-1-OH were virtually the same as those of the unfunctionalized polymer aPP-1 (Figure 2). These results demonstrate that the regiospecific, rhodium-catalyzed functionalization and subsequent oxidation of a model polypropylene occur without changing the molecular weight from that of the starting polymer.

B. Functionalization of a Commercial Atactic Polypropylene. The functionalization of a commercially produced atactic polypropylene (aPP-2, M_n = 16.1 kg/mol, PDI = 2.3) was conducted by the sequence of rhodium-catalyzed borylation and oxidation optimized for the functionalization of aPP-1. The borylated material (aPP-2-Bpin) was purified by filtering through a short plug of Celite and a short plug of silica gel to remove the remaining catalyst and small-molecule impurities. The ^1H, ^{11}B, and ^{13}C NMR spectra of aPP-2-Bpin were similar to those of aPP-1-Bpin.

Reaction of the borylated aPP-2-Bpin with basic hydrogen peroxide generated the hydroxylated aPP-2-OH. Extraction into hexanes and ethyl acetate and filtration through a short plug of

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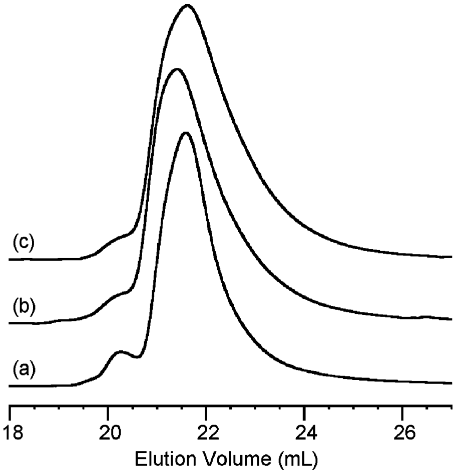

Figure 2. Size exclusion chromatogram (10 mg/mL THF) for (a) aPP-1 [$M_n = 44.0$, PDI = 1.2], (b) aPP-1-Bpin [$M_n = 46.6$, PDI = 1.3], and (c) aPP-1-OH [$M_n = 43.7$, PDI = 1.3] (Table 2, entry 1). M_n relative to polystyrene standards. aPP-1 = atactic polypropylene; aPP-1-Bpin = borylated atactic polypropylene; aPP-1-OH = hydroxylated atactic polypropylene; M_n = number-average molecular weight; PDI = polydispersity index.

silica gel removed any traces of boric acid and gave the pure, hydroxylated aPP-2 (aPP-2-OH) in 75−90% yield for the combination of borylation and oxidation. The NMR spectra of the isolated aPP-2-OH were similar to those of aPP-1-OH. Integration of the ^{1}H NMR spectrum of the sample generated from a 10:1 ratio of monomer to diboron compound showed that 1.3% of the side chains had been converted to hydroxymethyl groups. This value corresponds to an average of 5 hydroxyl groups per chain or 0.7 hydroxyl groups per 100 backbone carbons and is greater than that obtained for the model aPP. Characterization of the functionalized materials by SEC again showed that the borylation and oxidation did not lead to a change in molecular weight parameters.

The high-molecular-weight fraction ($M_n > \text{ca. } 10^3$) of a sample of material containing 0.82 mol % of the side chains functionalized with hydroxyl groups was again isolated by preparative SEC and analyzed by ^{1}H NMR spectroscopy. ^{1}H NMR spectroscopy showed that 0.84% of the side chains of the high-molecular-weight fraction were functionalized with hydroxyl groups, and the similarity of the degree of functionalization before and after separation by molecular weight again indicates that the hydroxyl groups are covalently attached to the polymer.

3. Functionalization of Commercial Semicrystalline Polypropylenes. A. Synthesis of Borylated and Hydroxylated Isotactic and Syndiotactic Polypropylenes. The sequence of polypropylene borylation and oxidation was extended to PP materials that are semicrystalline. While the favorable physical properties of the stereoregular, semicrystalline polypropylenes make these materials more important commercially, we were concerned that the high melting point of these polymers and the high viscosity of the melts would complicate efforts to extend the rhodium-catalyzed functionalization and subsequent oxidation to these substrates.Thus, we determined the effect of the type of rhodium catalyst, boron reagent, the molecular weight of the substrate, and the reaction stoichiometry on the degree of functionalization of the stereoregular polypropylenes. $(Cp^*RhCl_2)_2$, $Cp^*Rh(C_2H_4)_2$, and $Cp^*Rh(\eta^4\text{-}C_6Me_6)$ all catalyzed the borylation of commercial isotactic polypropylene, but like the borylation of the model PEP, reactions of the polypropylenes catalyzed by $Cp^*Rh(C_2H_4)_2$ and $Cp^*Rh(\eta^4\text{-}C_6Me_6)$ led to the generation of a higher degree of functionalization than did those catalyzed by $(Cp^*RhCl_2)_2$. This higher reactivity is likely to be due, in part, to the greater solubility of the arene and olefin complexes in the hydrocarbon polymer melts than that of the rhodium chloride. A change in the concentration of $Cp^*Rh(\eta^4\text{-}C_6Me_6)$ from 5 to 10 mol % did not affect the degree of functionalization.

The functionalization of the stereoregular polyolefins occurred at 200 °C over the course of 30 h with 5 mol % $Cp^*Rh(\eta^4\text{-}C_6Me_6)$ and 10 equiv of monomer repeat unit relative to B_2pin_2. Reactions of iPP-1 occurred with the highest degree of functionalization and were studied in the greatest depth (Table 2). After the functionalization reaction, the crude borylated stereoregular polymers were dissolved in hot toluene, and the low-molecular-weight impurities were removed by precipitation of the polymer in cold methanol. The isolated borylated polymer was then oxidized in a mixture of THF and H_2O with basic hydrogen peroxide to give the corresponding hydroxyl-containing polypropylenes. Because the borylated stereoregular polypropylenes of high molecular weight (iPP-2-Bpin, sPP-1-Bpin, and sPP-2-Bpin in Table 2) were essentially insoluble in THF, the oxidations of these polypropylenes with basic hydrogen peroxide were conducted with the materials suspended in a mixture of THF and water as fine particles.[42] The hydroxylated high-molecular-weight stereoregular polypropylenes were washed with distilled water to remove any residual boric acid, redissolved in hot toluene, and then isolated by precipitation in methanol. The mass recovery of this reaction was typically greater than 97%, based on the weight of the starting unfunctionalized polymer.

The borylation and oxidation sequence was amenable to the synthesis of functionalized isotactic polypropylene on relatively large scales. For example, this procedure was conducted on 100 g of iPP-1. Results from reactions on this scale paralleled those obtained from reactions on a smaller scale (see Experimental Section in the Supporting Information for details).

The effects of the choice of the boron reagent and the ratio of B_2pin_2 to monomer repeat unit on the degree of functionalization of the stereoregular polypropylenes were investigated. The level of functionalization with pinacolborane as the boron reagent was lower than that with bis(pinacolato)diboron. In addition, reactions with a 0.10 ratio of B_2pin_2 to monomer formed polymer with twice the degree of functionalization as reactions with a 0.030 ratio of B_2pin_2 to monomer (entries 6 and 8 of Table 2). Reactions conducted with even larger amounts of boron reagent, relative to monomer repeat unit, did not generate materials with more than 1% functionalized side chains. Consequently, high yields of borylated product can be obtained using this methodology, but the percentage of the methyl groups that were functionalized in the same chain was limited to roughly 1 mol % despite increasing the amount of boron reagent.

Studies of the effect of polymer molecular weight on the degree of functionalization showed that the highest degree of functionalization occurred with iPP-1, which has a lower molecular weight than the other steroregular polyolefins. ^{1}H NMR spectroscopy showed that up to 1.5 mol % of the methyl groups of iPP-1 were converted to hydroxymethyl groups. This

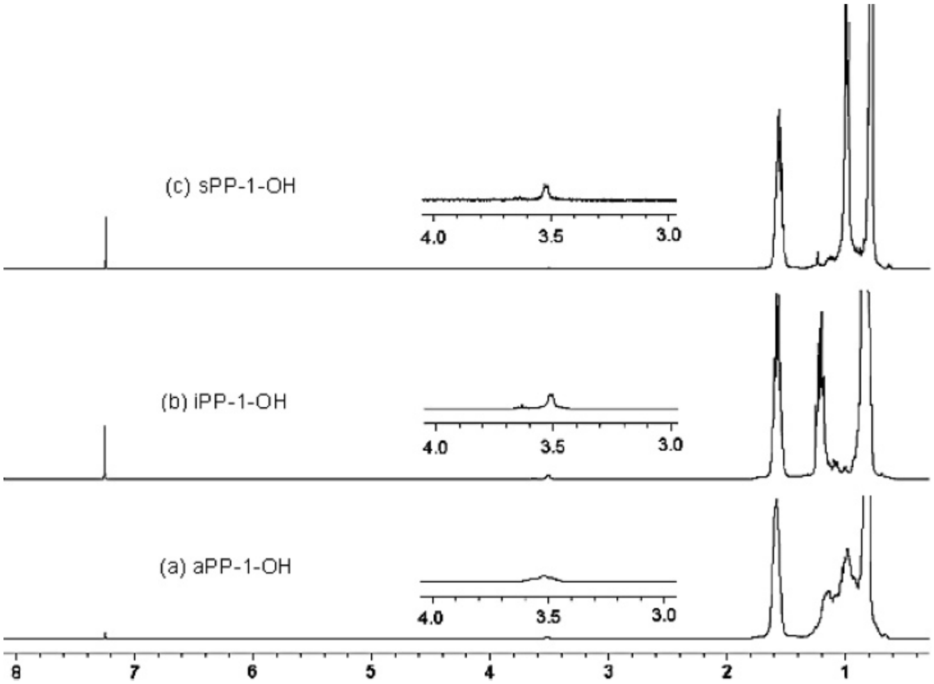

Figure 3. ^{1}H NMR spectra (delay time = 1 s, number of transients = 16, 25 °C) of hydroxylated atactic, isotactic, and syndiotactic polypropylenes: (a) aPP-1-OH [130 mg/mL $CDCl_3$], (b) iPP-1-OH [15 mg/mL $CDCl_3$], (c) and sPP-1-OH [15 mg/mL $CDCl_3$].

value corresponds to 6 hydroxyl groups per chain or 0.75 hydroxyl groups per 100 backbone carbons. The degree of functionalization of the polypropylenes of higher molecular weight was lower: 0.27 mol % of the side chains of iPP-2 was converted to hydroxymethyl groups (4.3 hydroxyls per chain or 0.13 hydroxyl per 100 backbone carbons), 0.35 mol % of the side chains of sPP-1 was converted to hydroxymethyl groups (3.3 hydroxyls per chain or 0.17 hydroxyl per 100 backbone carbons), and 0.31 mol % of the side chains of sPP-2 was converted to hydroxymethyl groups (4.9 hydroxyls per chain or 0.16 hydroxyl per 100 backbone carbons).

B. Characterization of the Borylated and Hydroxylated Isotactic and Syndiotactic Polypropylenes. The borylated and oxidized stereoregular polymers were characterized by NMR spectroscopy and high-temperature SEC.[52] The ^{1}H, ^{13}C, and ^{11}B NMR spectra of the borylated stereoregular polypropylenes contained resonances that were located at similar chemical shifts to those of the aPP materials. To assess the degree and type of functionalization, we focused on the NMR spectra of the functionalized iPP-1, which has a lower molecular weight than the other stereoregular polyolefins and is more soluble in organic solvents. This material also contained the highest percentage of functionalized side chains and, correspondingly, the most intense signals from the functional groups.

The ^{1}H NMR spectrum of iPP-1-Bpin contained a resonance at δ 1.25 that was assigned to the methyl groups of the Bpin unit. Similar to the ^{13}C NMR spectrum of the borylated PEP and of the aPP materials, the ^{13}C NMR spectrum of iPP-1-Bpin contained two signals of low intensity at δ 25 and δ 83 for the Bpin group. DEPT ^{13}C NMR spectroscopy confirmed that these signals were due to a methyl carbon and a quaternary carbon.

The ^{1}H NMR spectrum of iPP-1-OH contained a distinct doublet at δ 3.51, and the ^{13}C NMR spectrum contained a singlet at δ 67, corresponding to a hydroxymethyl group, as shown in Figure 3. Attached proton test (APT) ^{13}C NMR spectroscopy confirmed that this carbon was due to a methylene unit. The backbone carbons of iPP-1-OH located β and γ to the hydroxyl group generated signals in the ^{13}C NMR spectrum at δ 36 and δ 40 (see Supporting Information). The ^{13}C NMR spectrum of iPP-1-OH lacked resonances at δ 25 and δ 83 that would correspond to the alkyl-Bpin groups of the iPP-1-Bpin reactant. The absence of these signals indicated that the boryl groups of iPP-1-Bpin had been completely converted to hydroxyl groups, despite the heterogeneity of the oxidation process.

Like the functionalization of model and atactic polypropylenes, the rhodium-catalyzed functionalization of commercial stereoregular polyolefins occurred without significant degradation of the chain. The high temperature SEC data in Table 2 show that the relatively narrow PDI (2.1) and the value of the M_n of iPP-1 were unchanged throughout the borylation and oxidation processes (Table 2, entries 6–8; Figure 4). Furthermore, The glass transition temperature (−34 °C), melting point (116 °C), and percent crystallinity (17%) of an iPP sample, as determined by differential scanning calorimetry, were virtually identical to the glass transition temperature (−33 °C), melting point (119 °C), and percent crystallinity (14%) of the hydroxylated material. These data are consistent with insignificant changes in the material's molecular weight, tacticity, and propensity to form crystallites. Likewise, the functionalization of sPP-1 occurred without significant change to the molecular parameters of the polymer, regardless of the ratio of monomer to B_2pin_2 used in the borylation process (Table 2, entries 10 and 11).

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(52) We attempted to obtain data on the presence of hydroxyl groups by FT-IR spectroscopy, but the spectrum of iPP-1-OH was indistinguishable from that of iPP-1 because of the low concentration of hydroxyl groups. A similar lack of an infrared signal for a hydroxyl group was reported previously for a material prepared by oxidation of a product prepared by copolymerization of propylene and 5-hexenyl-9-BBN to provide a copolymer containing 0.5 mol % of 5-hexenyl-9-BBN units. Chung, T. C.; Rhubright, D.; Jiang, G. J. *Macromolecules* **1993**, *26*, 3467.

Table 3. Steric Effect on Functionalization of Side Chains of Polyolefins

entry	Rh catalyst	$[\text{monomer}]_0/[B_2\text{pin}_2]_0$ [a]	polyolefin			polyolefin-OH	
				side chain	M_n [b] (PDI [c])	OH [d] (%)	efficiency [e] (%)
1	$(Cp^*RhCl_2)_2$	14	PEE	Et	37 (1.04)	4.6	66
2	"	1	PEE	Et	37 (1.04)	14	14
3	$Cp^*Rh(\eta^4\text{-}C_6Me_6)$	20	PEP	Me	8.4 (1.1)	1.4	28
4	"	10	PEP	Me	8.4 (1.1)	1.7	17
5	"	20	aPP-2	Me	16.1 (2.3)	1.2	24
6	"	10	aPP-2	Me	16.1 (2.3)	1.3	13

[a] B_2pin_2 = bis(pinacolato)diboron. [b] M_n = number-average molecular weight in kg/mol determined by size exclusion chromatography with THF as eluent. Values are relative to polystyrene standards. [c] PDI = polydispersity index M_w/M_n. [d] mol % of CH_2OH relative to alkyl side chains. [e] Efficiency of functionalization (the percentage of hydroxyl group in the final polymer relative to the B_2pin_2 added).

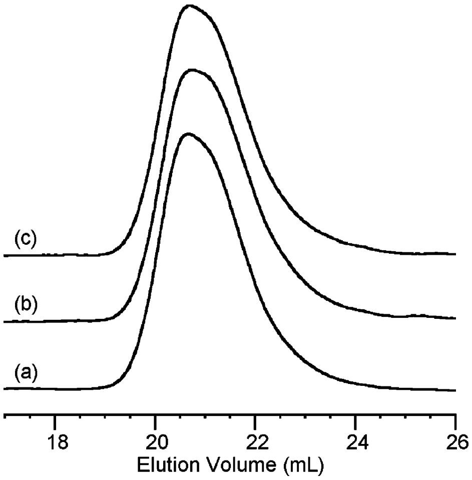

Figure 4. Size exclusion chromatogram (1 mg/mL 1,2,4-trichlorobenzene) for (a) iPP-1 [M_n = 17.6 kg/mol, PDI = 2.1], (b) iPP-1-Bpin [M_n = 15.8 kg/mol, PDI = 2.1], (c) iPP-1-OH [M_n = 15.8 kg/mol, PDI = 2.2] in entry 6 in Table 2. M_n relative to polystyrene standards. iPP-1 = isotactic polypropylene; iPP-1-Bpin = borylated isotactic polypropylene; iPP-1-OH = hydroxylated isotactic polypropylene; M_n = number-average molecular weight; PDI = polydispersity index.

4. Effect of Steric Hindrance, Polymer Molecular Weight, and Tacticity on the Functionalization Process. The rhodium-catalyzed reactions of materials with different molecular architectures and molecular weights revealed the effect of polymer structure on the efficiency and degree of functionalization. To determine the effect of the steric properties on the functionalization of materials with relatively similar concentrations of methyl groups, we compared reactions of poly(ethylethylene) PEE (PEE, a model polybutene prepared by hydrogenation of polybutadiene produced by anionic polymerization, M_n = 37 kg/mol, PDI = 1.1)[43] with those of PEP (M_n = 8.4 kg/mol, PDI = 1.1) and the polypropylenes (iPP-1: M_n = 17.6 kg/mol, PDI = 2.1. aPP-2: M_n = 16.1 kg/mol, PDI = 2.3). The methyl groups of the polypropylenes are the most hindered because they are attached to a branched carbon and are present on every other carbon. The methyl groups of PEP are less hindered because they are attached to every fourth carbon. The methyl groups of PEE are the least hindered because they are separated from the polymer backbone by a methylene group.

The PEE material was functionalized with B_2pin_2 at 150 °C in the presence of 2.5% $(Cp^*RhCl_2)_2$ with mole ratios of monomer units to the diboron reagent ranging from 14:1 to 1:1.[43] As summarized in Table 3, this reaction generated materials containing between 4.6 mol % and 14 mol % of the ethyl side chains functionalized with hydroxyl groups. These values correspond to an average of 31 and 95 hydroxyl groups per polymer chain and 2 to 7 hydroxyl groups per 100 backbone carbons. This was the highest degree of functionalization obtained, even though $(Cp^*RhCl_2)_2$ was used as catalyst. The reaction efficiencies for the borylation of PEE decreased from 66% to 14% as the mole ratio of monomer repeat unit to diboron reagent decreased.

This efficiency of the borylation of the PEE was higher than that for borylation of the more hindered PEP and of polypropylene, which led to a maximum conversion of 1.7 mol % of methyl side chains and an efficiency ranging from 15 to 30% for ratios of propylene repeat unit to B_2pin_2 ranging from 10 to 20. Reactions of polypropylenes and PEP materials possessing similar low molecular weights occurred with similar degrees of functionalization and reaction efficiencies. Thus, the frequency of the methyl groups along the polymer chain did not significantly affect the degree of functionalization. However, the length of the side chain did effect the degree of functionalization, and the reduced steric hindrance of the methyl groups in the ethyl side chains allowed for much more efficient functionalization reactions of PEE compared to PEP.

The tacticity, or the relative orientation of the methyl groups, of the polymer was found to have little effect on the efficiency of the borylation process. We have not compared the functionalization of polymers with the same molecular weight, varying only in tacticity, because of the lack of availability of the necessary materials. However, the data in Table 2 show that atactic and isotactic polypropylenes of similar molecular weight undergo reaction with similar efficiencies (Table 2 entries 3−5 vs entries 6−8).

The effect of molecular weight of the polymer was more pronounced than the effect of tacticity, but was less significant than the effect of the steric properties, on the ultimate degree of functionalization obtained. The degree and efficiency of the functionalization of polypropylenes decreased with increasing molecular weights, regardless of the tacticity of the material. In addition, the degree of functionalization of low-molecular-weight polypropylenes (aPP-2 and iPP-1) increased when the ratio of diboron reagent to monomer was increased, but the degree of functionalization of the high-molecular-weight polypropylenes increased little when the ratio of diboron reagent to monomer was increased from 0.03 to 0.1.

5. Graft Copolymers of Polypropylene and Polycaprolactone. Polymer blends provide a method to design a material with tailored properties; however, most combinations of polymers are immiscible and require the addition of a compatibilizer to achieve good dispersion of the minor component in the polymer matrix.[53] The mechanical properties of incompatible

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(53) Vasile, C., Ed. *Handbook of Polyolefins*; Marcel Dekkar Inc.: New York, 2000.

Scheme 2. Synthesis of Isotactic Polypropylene-*graft*-polycaprolactone

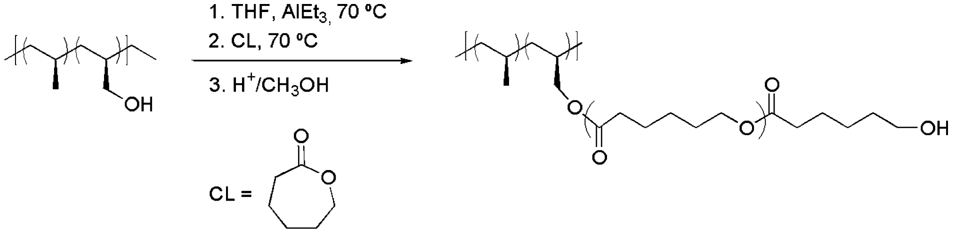

Table 4. Synthesis of Isotactic Polypropylene-*graft*-polycaprolactone[a]

entry	$[Al]_0$[b] (mM)	$[CL]_0$ (M)	$[CL]_0/[OH]_0$	[CL]/[OH][c]	$M_{n(graft)}$[c]	M_n[d]	M_w/M_n[d]	time (h)	yield[e] (%)
1	3.5	0.1	28	13	1.5	22.8	1.9	1	70
2	3.9[f]	0.5	60	24	2.7	34.3	3.1	3	92
3	1.2	0.2	55	36	4.0	56.6	1.8	20	100
4	1.5[g]	0.2	34	34	3.9	43.7	1.9	19	91
5	1.4	0.5	116	64	7.3	66.5	1.8	20	96
6	0.8	0.5	207	102	11.6	93.1	1.8	5	99
7	1.3	0.5	128	127	14.6	59.8	3.6	24	98
8	0.6	0.5	262	240	27.6	54.0	3.6	20	94

[a] Reaction conditions: hydroxylated isotactic polypropylene (iPP-1-OH), triethylaluminum ($AlEt_3$), THF, 2 h, 68 °C, caprolactone (CL) added, polymerization at 68 °C. [b] $AlEt_3$, $[OH]_0/[Al]_0 = 3$. [c] Number of repeat units per graft arm determined from the relative intensities of the end-groups of CL relative backbone resonances. [d] kg/mol. Determined by size exclusion chromatography (iPP-1-OH $M_n = 19.2$ kg/mol, $M_w/M_n = 2.3$). Values are relative to polystyrene standards measured using THF as the mobile phase. [e] Percent yield based on complete recovery of iPP and complete conversion of CL: 100 * [(mass of product − mass of iPP-1-OH)/mass of CL]. [f] $[OH]_0/[Al]_0 = 2$. [g] $[OH]_0/[Al]_0 = 4$.

binary blends are often limited by poor interfacial adhesion,[54] and graft copolymers have been used extensively to enhance the properties of such binary blends.[7,55−60] In this section, we report our investigations on the blends of two immiscible materials: polycaprolactone (PCL) and iPP[61] compatibilized by iPP−PCL graft copolymers prepared from iPP-1-OH.

Typically, graft copolymers are designed to be "mutually miscibile," with the two components of a blend. Therefore, to compatibilize iPP and PCL, we constructed graft copolymers with an iPP backbone and PCL side chains. These materials were prepared by the ring-opening polymerization of ϵ-caprolactone (CL) with a macroinitiator formed from triethylaluminum ($AlEt_3$) and the iPP-1-OH containing 1% hydroxymethyl groups prepared on a 100 g scale (Table 2, entry 7) (Scheme 2). Binary blends of iPP and PCL and ternary blends of iPP, PCL, and the graft copolymer were prepared with various ratios of the components. The thermal and mechanical properties of the polymer composites were then investigated.[62,36]

A. Synthesis and Characterization of Isotactic Polypropylene-*graft*-polycaprolactone. The reaction of the hydroxyl groups in iPP-1-OH with $AlEt_3$ produced aluminum alkoxides, which initiate ring-opening polymerization of cyclic esters,[63] and reaction of these alkoxides with caprolactone generated isotactic polypropylene-*graft*-polycaprolactone (iPP-*g*-PCL) (Scheme 2). The degree of polymerization of the PCL side chains was controlled by the reaction stoichiometry $[CL]_0/[OH]_0$ (Table 4). Our results were consistent with those obtained by Chung et al. for the ring-opening polymerization of CL by pendant hydroxyl groups generated from oxidation of a copolymer of propylene and 5-hexenyl-9-BBN (BBN = borabicyclononyl).[36] By performing the polymerization for different reaction times, we found that high conversion of CL to PCL was observed after 5 h with $[CL]_0 = 0.50$ M and $[AlEt_3]_0/[OH]_0 = 3$.

The iPP-*g*-PCL graft copolymers were characterized by ^1H NMR spectroscopy. Specifically, the ^1H NMR spectrum of the iPP-1-OH starting material contained a doublet at $\delta = 3.5$, corresponding to the methylene protons α to the hydroxyl group. The ^1H NMR spectrum of the graft copolymer contained a new resonance at $\delta = 3.6$, corresponding to the methylene protons α to the hydroxyl group at the end of the polycaprolactone side chains, and the resonance at 3.5 ppm for the starting material was absent. The appearance of this new resonance at δ 3.6 and the resonances characteristic of PCL indicated the formation of the graft copolymer (Figure 5).[64] The formation of graft copolymer was also confirmed by ^{13}C NMR spectroscopy. The resonance assigned to the carbon α to the hydroxyl group in iPP-1-OH at $\delta = 67.3$ was absent, and a new resonance at $\delta = 62.5$, which is a chemical shift typical for the carbon α to the hydroxyl end group in a PCL homopolymer, was observed.

Analysis of the graft copolymer by SEC showed that M_n of the graft copolymer (Table 4, entry 3, 56.6 kg/mol) was higher than that of the starting material (19.2 kg/mol) and that the PDI of the graft copolymer was relatively narrow (Figure 6). The theoretical M_n of this grafted polymer was estimated to be 42.9 kg/mol based on the M_n of iPP-1-OH (19.2 kg/mol), which had 5.9 hydroxyl groups per 455 repeat units (1.3 mol %), and the M_n of the grafted arms (5.9 arms × 4.0 kg/mol), determined by end group analysis. This value of M_n is smaller than that determined by SEC, most likely because of the conformational differences between a linear copolymer and a graft copolymer.[65]

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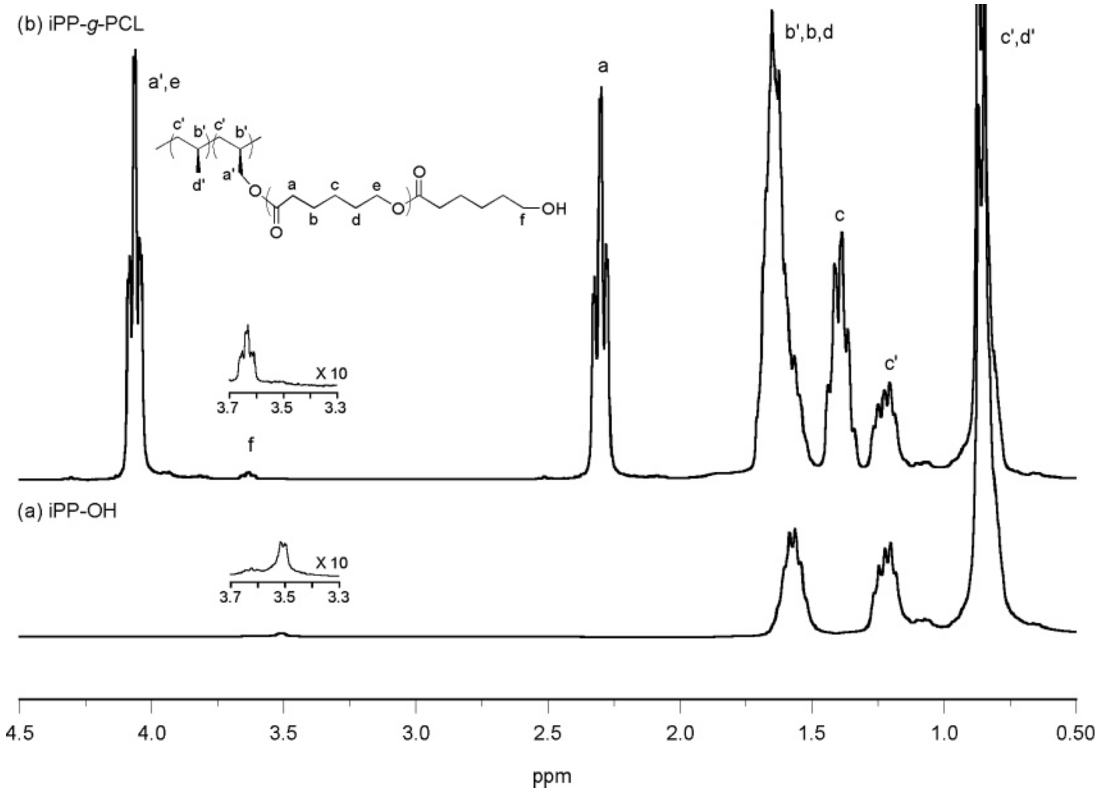

Figure 5. ^{1}H NMR spectrum of (a) hydroxylated isotactic polypropylene [25 °C, 16 transients, 0.75 wt % in $CDCl_3$, delay time = 20.0 s] and (b) isotactic polypropylene-graft-polycaprolactone [50 °C, 16 transients, 0.75 wt % in $CDCl_3$, delay time = 15.0 s] from entry 3 from Table 4.

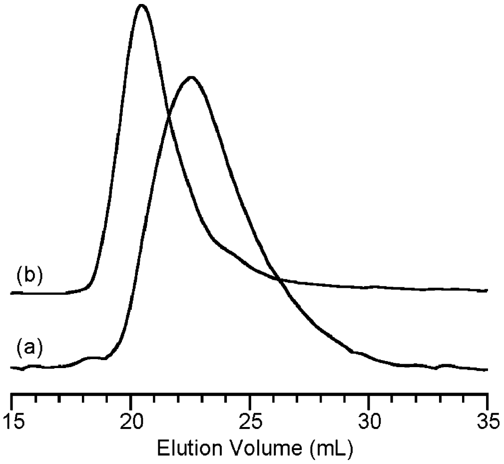

Figure 6. Size exclusion chromatogram of (a) hydroxylated isotactic polypropylene [M_n = 19.2 kg/mol, PDI = 2.3] and (b) isotactic polypropylene-graft-polycaprolactone [M_n = 56.6 kg/mol, PDI = 1.8] from entry 3 in Table 4.

The thermal properties of the graft copolymers were analyzed by differential scanning calorimetry (DSC). Two different glass transition temperatures (T_g) were observed in the DSC data that corresponded to typical thermal transitions for the parent homopolymers: iPP phase (−29 to −34 °C) and PCL phase (−61 to −63 °C) (Table 5). The appearance of two glass transition temperatures is consistent with microphase separation of the two immiscible materials.[61]

Table 5. Thermal Properties of the iPP−PCL Graft Copolymers

entry	iPP-OH/PCL[a,b]	$T_{g(PCL)}$[c]	$T_{g(iPP)}$[c]	$T_{m(PCL)}$[c,d]	$T_{m(iPP)}$[c,d]
1	0/100	−61		55	
2	10/90	−56	−31	57	112
3	20/80	−63	−29	57	107
4	37/63	−61	−32	55	108
5	55/45	−63	−32	54	112
6	65/35	−62	−32	56	106
7	85/15	−60	−33	44	113
8	100/0		−34		119

B. Melt Blends of Isotactic Polypropylene and Polycaprolactone with Isotactic Polypropylene-*graft*-polycaprolactone. To investigate the effect of adding the graft copolymer iPP-*g*-PCL to a binary blend of iPP and PCL, we generated melt blends of iPP (97 kg/mol) and PCL (101 kg/mol) with and without added graft copolymer. These blends were prepared in a Haake Rheomix 600 batch mixer at 190 °C, with 15 min of mixing at 50 rpm.[60]

Graft copolymers with an iPP backbone (M_n = 19.2 kg/mol) and ca. 6 graft arms of PCL with M_n values of about 4, 15, and 28 kg/mol (entries 4, 7, and 8 from Table 4) were investigated as potential compatibilizers. Binary blends of iPP and PCL and ternary blends of iPP, PCL, and iPP-*g*-PCL were prepared in various compositions. Analysis of the thermal and mechanical properties of these composite materials showed that the impact strength and the tensile toughness of the compatibilized PCL/iPP composites were similar to those of the composites generated without the graft copolymer. We suspect that the low molecular weight of the polypropylene backbone in the graft copolymer provided inadequate entanglements at the iPP/PCL interface, and thus these composites did not show improved mechanical properties.[55,60,66,67]

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To investigate further these composite materials, we analyzed the blend morphology of several cryofractured samples by scanning electron microscopy (SEM). In micrographs of an 80/20 iPP/PCL blend specimen without graft copolymer, two distinct phases could easily be distinguished; spherical PCL particles were dispersed in the iPP matrix. This was expected given the demonstrated incompatibility of the two materials. In contrast, the micrographs of the 80/20 iPP/PCL blends with graft copolymer were nearly featureless, and it was difficult to identify two distinct phases. While the inability to distinguish the two phases is consistent with effective compatibilization of the iPP/PCL blend, the particle size and distribution were difficult to evaluate quantitatively with the micrographs. For a 50/50 iPP/PCL blend, two distinct phases could be seen in the SEM images of the cryofractured sample, independent of whether the block copolymer was used.

To examine further the effect of the graft copolymer on compatibilization, particle size, particle size distribution, and particle dispersion, the PCL component was etched from several cryofractured blends, and the resulting materials were analyzed using SEM (Figure 7). We removed the PCL from the monolith of the blend consisting of 48/48/4 iPP/PCL/iPP-*g*-PCL by treatment with acetone, which dissolves PCL but not iPP. The SEM micrograph of this material is shown in Figure 7a. The SEM shows voids that were templated by the PCL particles. The interconnection of these voids suggests a cocontinuous morphology.

The surface PCL particles of cryofractured samples of 80/20 PP/PCL blends (80/20/0 and 76/16/8 iPP/PCL/iPP-*g*-PCL) were also removed by selective dissolution of PCL. SEM micrographs of the etched 80/20 blends indicate that the particles in the composites with and without graft copolymer as a compatibilizer are unevenly dispersed but that the particles in the blend with the graft copolymer are smaller (largest particles on the order of 1 μm, Figure 7c) than those of the binary blend (largest particle > 3 μm) (Figure 7b). Thus, the images of the etched samples support the conclusion that the graft copolymer is an effective compatibilizer for iPP and PCL blends.

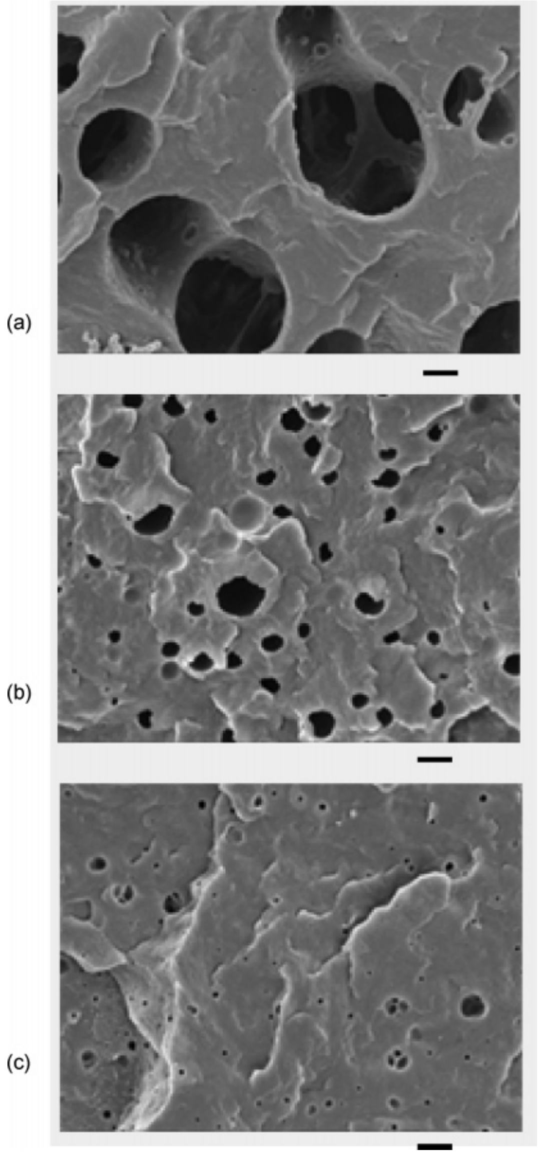

Figure 7. Scanning electron microscopy images of PCL-etched cryofractured specimens of binary (isotactic polypropylene/polycaprolactone [iPP/PCL]) and ternary blends (iPP/PCL/iPP-*graft*-PCL) (×5000) scale bar = 1 μm. (a) 48/48/4, (b) 80/20, and (c) 76/18/8.

Conclusions

Regiospecific functionalization of model and commercially available polypropylenes was achieved by the combination of rhodium-catalyzed borylation of the methyl C−H bonds of alkanes and oxidation of the resulting boron-containing polymers. In contrast to previous modifications of polyolefins, the borylation and oxidation did not change the molecular weight parameters of the polypropylenes. The efficiency of the borylation process depended on the molecular weight of the polymers and on the ratio of diboron reagent to monomer unit, but not on the tacticity of polymer. Because this regiospecific functionalization of polypropylene was unaffected by the tacticity of the polymer, it provides a method to prepare functionalized polyolefins from a range of commercial polyolefins.

We have also synthesized graft copolymers, such as polypropylene-*graft*-polycaprolactone, from the hydroxylated isotactic polypropylenes prepared by the rhodium-catalyzed methodology. The resulting iPP-*g*-PCL copolymers were characterized by NMR spectroscopy, DSC, and SEC, revealing that the graft polymerization generates materials with molecular weights that are controlled by the reaction stoichiometry and with molecular weight distributions that are narrow. The resulting copolymers that were prepared with polypropylenes as starting materials compatibilize immiscible blends of polypropylene and polycaprolactone, as shown by SEM micrographs of PCL-etched cryofractured samples.

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Supporting Information Available: Experimental section and APT ^{13}C NMR spectra of iPP-1 and iPP-1-OH. This material is available free of charge via the Internet at http://pubs.acs.org.

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