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# Synthesis and Functionalization of Unsaturated Polyethylene: Poly(ethylene-*co*-1,4-hexadiene)

**T. C. Chung,* H. L. Lu, and C. L. Li**[†]

*Department of Materials Science and Engineering, The Pennsylvania State University, University Park, Pennsylvania 16802*

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ABSTRACT: This paper describes the synthesis of poly(ethylene-co-1,4-hexadiene) copolymers, which are useful intermediates for the preparation of functionalized linear low-density polyethylene (LLDPE-f). Three catalyst systems, including one heterogeneous catalyst ($TiCl_3{\cdot}AA/Et_2AlCl$) and two homogeneous metallocene catalysts ($Cp_2ZrCl_2$ and $Et(Ind)_2ZrCl_2$ with MAO), were used in the copolymerization reaction between ethylene and 1,4-hexadiene. In general, the homogeneous catalysts are much more effective than their heterogeneous counterparts in the incorporation of diene monomers in PE structure. Especially, the single-site $Et(Ind)_2ZrCl_2$/MAO catalyst with a strained geometry provides unsaturated PE with narrow molecular weight distribution and controllable diene concentration. It is not expected that the catalyst activity systematically increases with the concentration of 1,4-hexadiene. Employing a combination of unsaturated PE and borane reagents, many LLDPE-f polymers, containing borane, hydroxy, amino, and silane groups, were obtained despite heterogeneous reaction conditions. Apparently the double bonds in the side chain are located in the amorphous phase and are available for reaction with reagents.

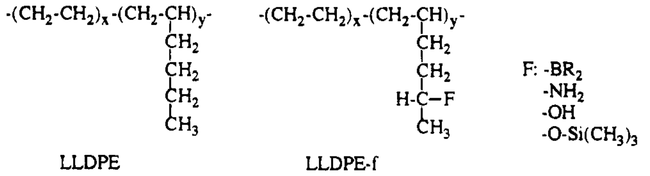
## Introduction

The lack of functional (reactive) groups in polyolefins has significantly limited many of their end uses, particularly those in which adhesion, dyeability, paintability, printability, or compatibility with other polymers is paramount. It has long been a scientific challenge in exploring the routes to functionalize polyolefins,[1–4] especially polyethylene and polypropylene. These functionalized polyolefins can serve as interfacial modifiers to improve their adhesion to and compatibility with other materials.

In general, there are two routes to the functionalization of polymers, including direct copolymerizations with functional monomers and chemical modifications of preformed polymers. Unfortunately, Ziegler–Natta catalysts used in the preparation of polyolefins are normally incapable of incorporating functional group-containing monomers because of catalyst poisoning.[5] In the past few years, we have successfully developed a new approach by using borane monomers[6,7] which can be copolymerized with α-olefins in Ziegler–Natta polymerization. Many polyolefins with a broad range of compositions[8,9] have been obtained with many desirable physical properties.

On the other hand, modification reactions of polyolefins are usually accompanied by some undesirable side reactions, such as cross-linking and degradation[10] of the polymer backbone. In addition, the control of functional group concentration and homogeneity in the polyolefin backbone is usually very difficult. Recently, there have been several successful examples of unsaturated polymers,[11,12] with the double bonds at the chain ends[13] or pendant along the polymer backbone,[14] as the "reactive" prepolymers for subsequent modification reactions resulting in functionalized products.

In this paper, we adopt a two-step approach involving (i) the preparation of unsaturated polyethylene, resulting from a copolymerization reaction of ethylene and 1,4-hexadiene using $Et(Ind)_2ZrCl_2$/MAO catalyst and (ii) subsequent functionalization by borane chemistry. The unique combination of comonomer, single-site catalyst, and borane reagents provides the route to prepare functionalized polyethylene with a broad range of concentrations and compositions of functional groups, such as $NH_2$ and OH. The resulting functionalized polyethylene (LLDPE-f) is structurally similar to that of linear low-density polyethylene (LLDPE) as shown below:



It is very interesting to note the advantages of 1,4-hexadiene as a comonomer. (i) The low boiling point offers the possibility of using gas phase copolymerization processes. (ii) The unsymmetrical diene provides selective copolymerization at the α-olefin group. Therefore, a high concentration of diene comonomer can be incorporated into the PE structure without cross-linking reactions. (iii) The internal double bonds in PE result in desirable borane moieties, containing secondary C–B bonds in the side chain of PE, after hydroboration reactions. The secondary C–B bond can be quantitatively converted to various functional groups. The complete interconversion of borane groups to other functionalities is essential to obtain processible PE products.

## Results and Discussion

Equation 1 illustrates the reaction scheme which includes two major steps: (i) the copolymerization of ethylene and 1,4-hexadiene and (ii) the subsequent interconversion of unsaturated groups to various functional groups by using borane reagents.

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* Author to whom all correspondence should be addressed.

[†] Permanent address: Department of Chemistry, Chung Yuan University, Chung Li, Taiwan.

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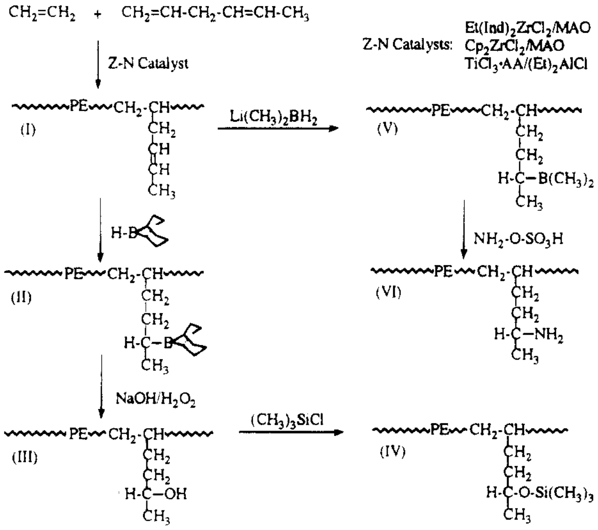
**Table 1. Summary of Copolymerization Reactions between Ethylene ($m_1$) and 1,4-Hexadiene ($m_2$)**

| run no. | catal type[a] | comonomer feed | | reaction temp (°C) | reaction time (min) | catal activ[c] (kg/mol·h) | diene in copolymer (mol %) |
|---|---|---|---|---|---|---|---|
| | | $m_1$[b] (psi) | $m_2$ (mol/L) | | | | |
| A-1 | I | 45 | 0.244 | 30 | 70 | 0.67 | 0 |
| B-1 | II | 45 | 0 | 30 | 70 | 326 | 0 |
| B-2 | II | 45 | 0.244 | 30 | 70 | 606 | 2.0 |
| B-3 | II | 45 | 0.488 | 30 | 70 | 1278 | 2.8 |
| B-4 | II | 45 | 0.244 | 65 | 60 | 1960 | 2.2 |
| C-1 | III | 45 | 0 | 30 | 60 | 644 | 0 |
| C-2 | III | 45 | 0.061 | 30 | 60 | 1048 | 1.8 |
| C-3 | III | 45 | 0.122 | 30 | 60 | 1480 | 2.7 |
| C-4 | III | 45 | 0.244 | 30 | 30 | 3828 | 3.4 |
| C-5 | III | 45 | 0.244 | 30 | 60 | 2320 | 3.3 |
| C-6 | III | 45 | 0.244 | 30 | 90 | 1960 | 3.5 |
| C-7 | III | 45 | 0.244 | 30 | 120 | 1550 | 4.0 |
| C-8 | III | 45 | 0.488 | 30 | 60 | 5120 | 4.6 |

[a] Catalysts: $TiCl_3{\cdot}AA/Et_2AlCl$ (I), $Cp_2ZrCl_2/MAO$ (II), and $Et(Ind)_2ZrCl_2/MAO$(III). [b] Corresponding to 0.38 mol/L. [c] Kilogram of copolymer per mole of Zr per hour.



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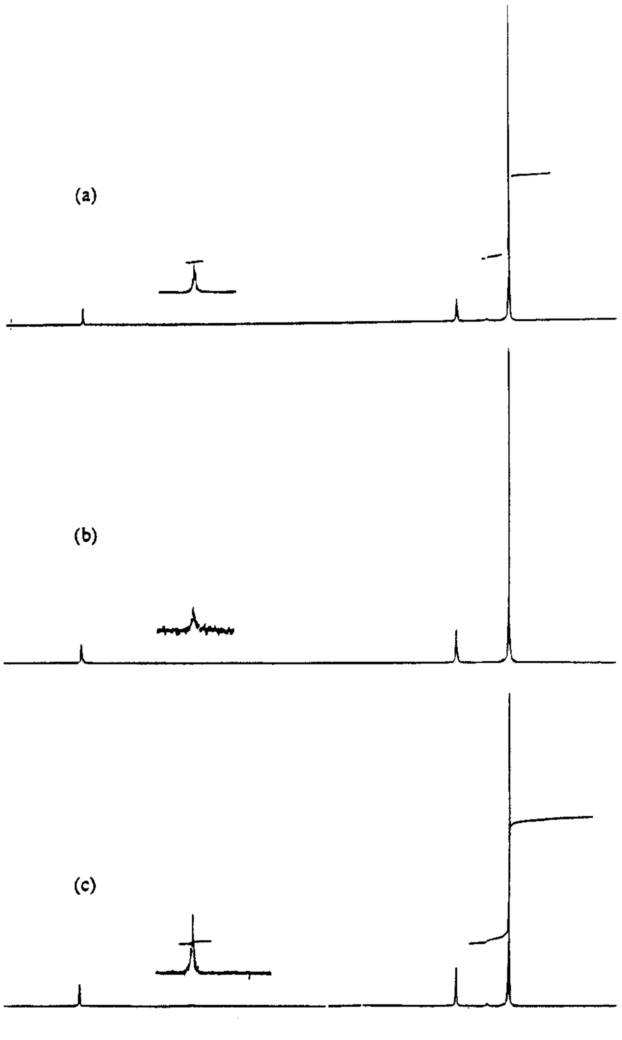

**Figure 1.** The ${}^1H$ NMR spectra of poly(ethylene-*co*-1,4-hexadiene) copolymers, containing (a) 1.40 (b) 2.84, and (c) 4.63 mol % 1,4-hexadiene.

**Copolymerization Reactions of Ethylene and 1,4-Hexadiene.** The copolymerization reactions were carried out in a Parr reactor under $N_2$ atmosphere. Three catalyst systems, including one heterogeneous $TiCl_3{\cdot}AA/(Et)_2AlCl$ catalyst (I) and two homogeneous metallocene $Cp_2ZrCl_2$ (II) and $Et(Ind)_2ZrCl_2$ (III) with MAO catalysts, were used in the copolymerization reactions of ethylene and 1,4-hexadiene monomers. Usually, the reaction was initiated by charging catalyst solution into the mixture of 1,4-hexadiene and ethylene, and a constant ethylene pressure was maintained throughout the polymerization process. The copolymerization was terminated by addition of dilute $HCl/CH_3OH$ solution. Table 1 summarizes the experimental results. Overall, the homogeneous zircorocene/MAO catalysts show satisfactory reactivities at ambient temperature. It is very unexpected that the catalyst activity systematically increases with the concentration of 1,4-hexadiene, especially, in the $Et(Ind)_2ZrCl_2/MAO$ catalyst system. The catalyst activity attains a value of more than $5 \times 10^6$ g of copolymer (mol of Zr h)[15] in run C-8 (a copolymerization of ethylene and diene with mole ratio of 3/4), which is ~8 times the value for the homopolymerization of ethylene in run C-1 under similar reaction conditions. By comparing runs from C-4 to C-7, the diene incorporation in PE copolymer seems ineffective for a long period of reaction time. About 80% of 1,4-hexadiene monomers was incorporated into the PE copolymer after a 2 h reaction time in run C-7. However, the catalyst activity slightly decreases with an increase in reaction time, which may due to the decrease of diene concentration.

The 1,4-hexadiene concentration in each PE copolymer was determined by ${}^1H$ NMR spectra, as shown in Figure 1. The integrated intensity ratio between the chemical shift at 5.5 ppm, corresponding to the $CH=$ group in the diene unit, and the chemical shift at 1.4 ppm, corresponding to $CH_2$ group in ethylene unit, provides the copolymer composition. The heterogeneous catalyst $TiCl_3{\cdot}AA/Et_2AlCl$ performs very poorly in the incorporation of 1,4-hexadiene in polyethylene, which must be due to the extreme difference in the comonomer

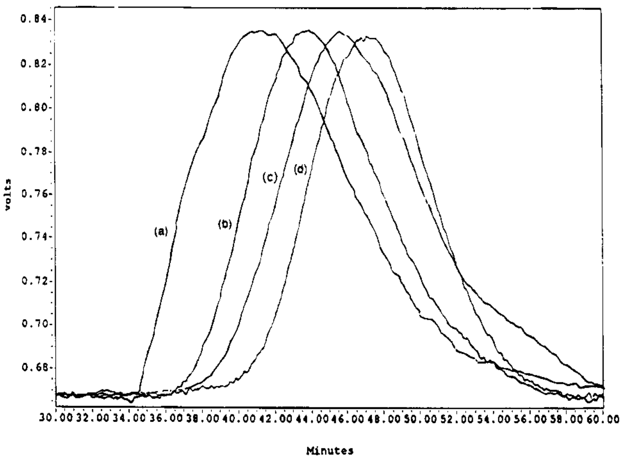

**Figure 2.** GPC curves of (a) HDPE (C-1) and three (ethylene-*co*-1,4-hexadiene) copolymers with (b) 1.2 (c) 1.8 (C-2), and (d) 4.6 (C-8) mol % of diene.

**Table 2. Molecular Structures of Poly(ethylene-*co*-1,4-hexadiene) Copolymers**

| run no. | $M_w \times 10^{-3}$ (g/mol) | $M_w/M_n$ | $T_m$ (°C) | $\chi_c$ (%) |
|---|---|---|---|---|
| B-1 | 290.7 | 6.64 | 133.8 | 65.0 |
| B-2 | 64.9 | 3.37 | 120.3 | 39.7 |
| B-3 | 47.5 | 2.06 | 113.6 | 33.9 |
| B-4 | 17.1 | 3.37 | 121.0 | 48.7 |
| C-1 | 250.4 | 3.67 | 136.8 | 53.9 |
| C-2 | 68.2 | 4.08 | 121.1 | 40.1 |
| C-3 | 42.9 | 4.36 | 115.8 | 31.3 |
| C-4 | 70.5 | 3.77 | 107.0 | 26.8 |
| C-5 | 41.3 | 2.88 | 110.0 | 29.6 |
| C-6 | 42.3 | 2.76 | 107.9 | 27.3 |
| C-7 | 43.0 | 3.20 | 108.4 | 30.5 |
| C-8 | 49.8 | 2.51 | 106.7 | 27.9 |

reactivities. The limited spatial opening at the active site results in the extreme sensitivity of reactivity to the size of monomer; the smaller the size the higher the reactivity. On the other hand, the homogeneous zirconocene/MAO catalyst systems are much more effective. A relatively high concentration of 1,4-hexadiene units were incorporated into the PE copolymers. The soluble active sites provide the flexibility to accommodate both monomer insertions. It is important to note that the single-site $Et(Ind)_2ZrCl_2$/MAO catalyst offers the best route to prepare the unsaturated PE copolymers with narrow molecular weight distribution and controllable diene concentration. The strained ligand geometry provides good spatial freedom with well-defined structure at the active site for the monomer to insert into the growing chain end.

**GPC and DSC Studies of Poly(ethylene-*co*-1,4-hexadiene) Copolymers.** The molecular weights of the copolymers were determined by high-temperature GPC measurements at 135 °C with trichlorobenzene as the mobile phase. Figure 2 compares GPC curves of a PE homopolymer and several poly(ethylene-*co*-1,4-hexadiene) copolymers prepared by both $Cp_2ZrCl_2$/MAO and $Et(Ind)_2ZrCl_2$/MAO catalysts. Overall, the copolymer molecular weight is significantly dependent on the presence of 1,4-hexadiene comonomers. The molecular weight distribution ($M_w/M_n$) was in the range of 2.5–4.5 in most cases. The complete list of molecular weight information of homo- and copolymers (shown in Table 1) is summarized in Table 2. All high-density PE homopolymers produced by these three catalyst systems, at ambient temperature and 45 psi ethylene pressure, are quite high molecular weight polymers, with $M_w > 250\,000$ g/mol. The addition of a small quantity of diene comonomers, such as ~15 mol % of diene in run C-3, sharply decreases the molecular weight to a quarter ($M_w \sim 68\,200$ g/mol), despite the significant increase in catalyst efficiency as shown in Table 1. The molecular weight becomes less sensitive to the quantity of diene as shown in runs C-2, C-3, C-4, and C-8. In fact, as seen in run C-8, with initial mole ratio of ethylene/diene = 3/4 produces a copolymer with the weight-average molecular weight still over 49 000 g/mol and fairly narrow molecular weight distribution with $M_w/M_n = 2.5$. By comparing runs C-4, C-5, and C-6, one sees that the molecular weight distribution decreases slightly with longer reaction time. The overall results seem to indicate that a chain transfer reaction to 1,4-hexadiene takes place and produces a new active site which has higher activity than the initial active site.

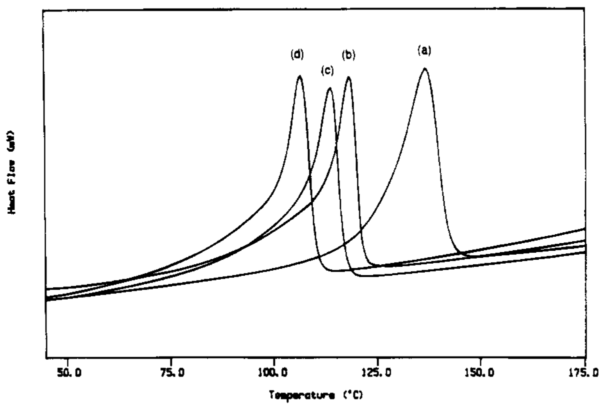

**Figure 3.** DSC curves of (a) HDPE (C-1) and three poly(ethylene-*co*-1,4-hexadiene) copolymers with (b) 1.8 (C-2), (c) 2.7 (C-3), and (d) 4.6 (C-8) mol % diene.

The crystalline structure of unsaturated PE was studied by differential scanning calorimetry (DSC). Figure 3 shows the comparison of DSC curves between high-density PE (C-1) and several poly(ethylene-*co*-1,4-hexadiene) copolymers (C-2, C-3, and C-8), all of them prepared by $Et(Ind)_2ZrCl_2$/MAO catalysts. As expected, both the melting point ($T_m$) and crystallinity ($\chi_c$) of copolymer are dependent on the density of side chains; the higher the density the lower the $T_m$ and $\chi_c$. In each copolymer, only a single peak is shown with slight tailing in the low melting point fraction. The nature of the low melting point fraction is not very clear and may be related to molecular weight or/and side-chain density. A combination of temperature-rising elution fractionation (TREF) with GPC and NMR measurements is currently under investigation and will provide three-dimensional characterization of molecular structure in each $T_m$ fraction. The melting point peak ($T_m$) and crystallinity ($\chi_c$) are compared in Table 2. The crystallinity ($\chi_c$) of copolymer was calculated from fusion enthalpy according to the following equation: $\chi_c = H_f/H_f^\circ \times 100$, where $H_f$ and $H_f^\circ$ (66 cal/g)[16] are the fusion enthalpies of copolymer and fold-chain polyethylene, respectively. Each copolymer pair (B-2/C-2 and B-3/C-3) with similar molecular weight and side-chain density shows similar crystallinities, with very little influence of $Et(Ind)_2ZrCl_2$/MAO and $Cp_2ZrCl_2$/MAO catalysts. Sample C-8, with an average of 1 side chain per 22 ethylene units, still possesses 28% crystallinity with $T_m$ = 106 °C.

**Functionalization of Poly(ethylene and 1,4-hexadiene) Using Borane Reagents.** The hydroboration reactions were carried out under heterogeneous reaction conditions by suspending the powder form of poly(ethylene-*co*-1,4-hexadiene) in THF solvent. Two dialkylborane reagents, e.g., lithium dimethylboro-

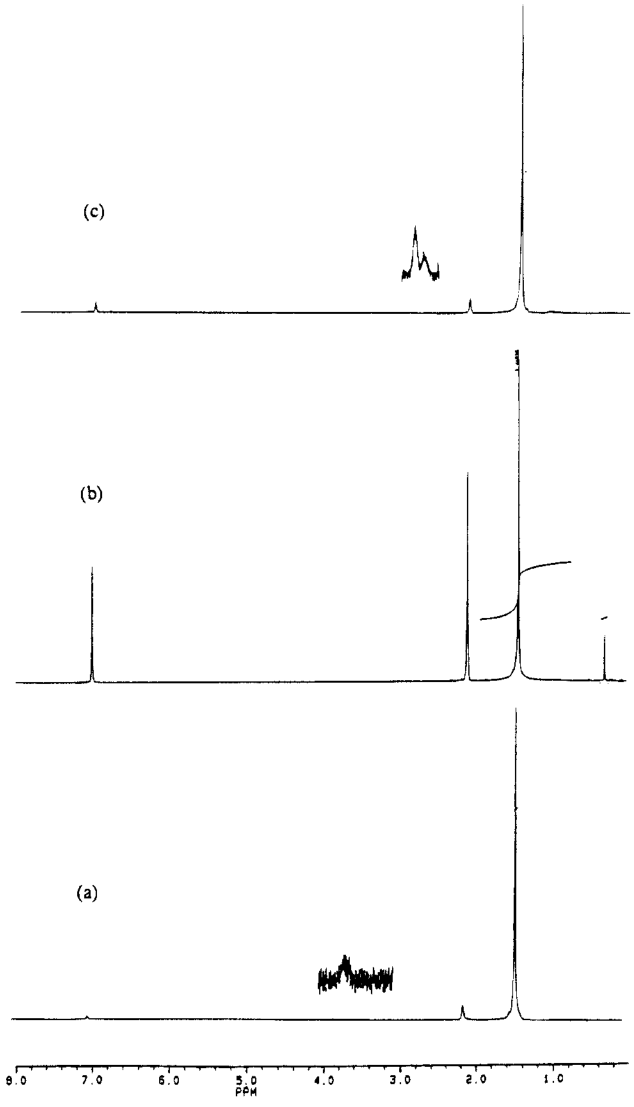

**Figure 4.** $^1H$ NMR spectra of functionalized PE copolymers containing (a) hydroxy, (b) silane, and (c) amino groups.

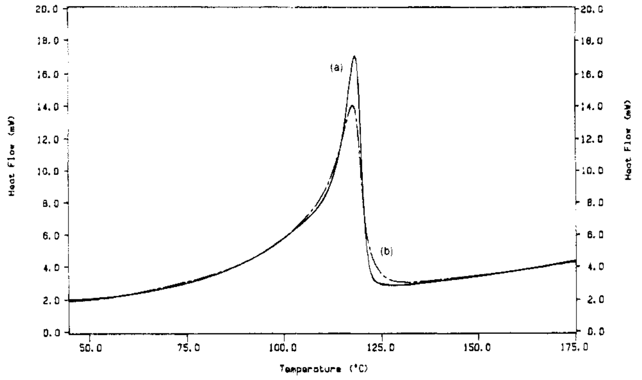

**Figure 5.** DSC comparison of poly(ethylene-*co*-1,4-hexadiene) copolymers (a) before and (b) after functionalization.

hydride and 9-borabicyclononane (9-BBN), were used in the hydroboration reactions. To ensure complete reaction of the internal double bonds, the reaction mixture was stirred at 65 °C for 3 h. The borane-containing copolymers are stable for long periods of time as long as $O_2$ is excluded. As illustrated in eq 1, the alkyl-9-BBN groups in the polymers were oxidized using $NaOH/H_2O_2$ reagents at 40 °C for 3 h. Figure 4a shows the $^1H$ NMR spectrum of hydroxylated PE (PE-OH), which was derived from sample C-2 with 1.8 mol % unsaturated side chains. The concentration of the unsaturated monomer units, corresponding to the chemical shift at 5.5 ppm, disappears to the limit of NMR sensitivity and exhibits a secondary alcohol methine peak, appearing at 3.6 ppm. The hydroxy groups in PE-OH can be further converted to silane groups by reacting with chlorotrimethylsilane. As shown in Figure 4b, silation was complete, with the disappearance of the secondary alcohol methine peak at 3.6 ppm and the appearance of $SiCH_3$ around 0.3 ppm. Apparently, both hydroboration and oxidation reactions were not inhibited by the insolubility of polyethylene. The efficacy of the reaction must be due to the high surface area of the reacting sites. While some of the polyethylene segments are crystallized, the side chains containing the double bonds are expelled into the amorphous phase which is swellable by the appropriate solvent during the reaction. In addition, the high reactivities in both hydroboration and oxidation reactions certainly enhance the efficiency of functionalization. All three B−C bonds are quantitatively converted to B−OH and C−OH groups. Similar results were also observed in the corresponding polypropylene cases.[17]

The amination reactions of trialkylboranes are usually not quantitative;[18] only one or two B−C bonds in trialkylborane molecule can be interconverted to $C-NH_2$ groups. The borane adducts after partially interconversion become too stable to continue the amination process. To assure the B−C bond joined to the polymer side chain is interconverted, selective amination is essential. Lithium dimethylborohydride was therefore used to provide two blocking methyl groups during the amination reaction. As shown in Figure 4c, the aminated PE shows only two new chemical shifts around 2.8 ppm, corresponding to two secondary amino methine ($C\mathit{H}NH_2$) groups located at the 4- and 5-position of the 1,4-hexadiene unit. The amino group-containing PE is completely soluble in toluene at high temperature.

Figure 5 compares the DSC curves before and after hydroxylation reaction of C-2 copolymer. Both samples underwent the same thermal history. There is no significant change in the crystalline structure after functionalization. The GPC study also shows no changes in the molecular weight and molecular weight distribution of copolymers. The borane reagents seem to provide a clean and effective route to the functionalization of polyethylene copolymers despite the semicrystalline structure. The concentration of functional groups in PE is essentially controlled by the quantity of borane reagents as well as the percentage of double bonds in PE copolymer.

## Experimental Details

**Instrumentation and Materials.** All room- and high-temperature $^1H$ NMR spectra were recorded on a Bruker AM-300 spectrometer with DISNMR software. Usually, the polyethylene copolymer was dissolved in *o*-xylene-$d_8$ at 110 °C. Differential scanning calorimetry (DSC) was measured on a Perkin-Elmer DSC-7 instrument controller. The DSCs were measured from 30 to 180 °C with a heating rate of 20 °C/min. The molecular weight was determined using a Waters 150C which was operated at 135 °C. The columns used were $\mu$Styragel HT of $10^6$, $10^5$, $10^4$, and $10^3$ Å. A flow rate of 0.7 mL/min was used, and the mobile phase was trichlorobenzene. Narrow molecular weight polyethylene samples were used as standards.

Ethylene bis(indenyl)zirconium dichloride ($Et(Ind)_2ZrCl_2$) was prepared as described in the literature.[19] $Cp_2ZrCl_2$ (Aldrich), $TiCl_3 \cdot AA$ (Alfa), MAO (Ethyl), and $Et_2AlCl$ (Aldrich) were purchased from commercial sources and used as received. High purity grade ethylene (MG Industries) was used as received. 1,4-Hexadiene (Wiley Organics) was dried over $CaH_2$

before distillation. HPLC grade tetrahydrofuran and toluene were deoxygenated by argon sparge before refluxing for 48 h and then distilled from their respective deep blue or purple sodium anthracenide solution under argon. Borane reagents, lithium dimethylborohydride and 9-borabicyclononane, were used as is from Aldrich.

**Synthesis of Poly(ethylene-*co*-1,4-hexadiene).** The copolymerization reactions were conducted in a Parr 450 ml stainless autoclave equipped with a mechanical stirrer. The following typical example describes the general procedure. In an argon-filled drybox, 4.0 g of 1,4-hexadiene, 100 mL of toluene, and 1.5 g of MAO (30 wt % in toluene) were placed in the reactor. The sealed reactor was then moved out from the drybox and was purged with ethylene gas at constant 45 psi pressure. After the temperature reached 30 °C, the catalyst solution of 2.09 mg (5 $\mu$mol) of $Et(Ind)_2ZrCl_2$ in 2 mL of toluene was added under ethylene pressure to catalyze the copolymerization. Additional ethylene was fed continuously into the reactor to maintain a constant pressure of 45 psi during the whole course of the copolymerization. After a predetermined reaction time, the reaction was terminated by addition of 100 mL of dilute solution of HCl in methanol. The polymer was isolated by filtration and washed with methanol before drying under vacuum.

**Hydroboration and Functionalization.** A 2.0 g sample of poly(ethylene-*co*-1,4-hexadiene) containing ~3 mol % diene monomer was placed in a Schlenk flask with 20 mL of THF and 80 mL of toluene. A solution of 0.510 g of 9-BBN in 10 mL of THF was added to the polymer dispersion. The flask was sealed and heated to 65 °C for 3 h. At that temperature, the polymer had completely dissolved. Upon cooling, the polymer precipitated from the solution. At lower temperatures, the polymer only swells and the reaction time must be increased to ~6 h. In the drybox, the Teflon valve was replaced by a rubber septum to allow addition of aqueous reagents under $N_2$ outside the box. The polyborane dispersion was complexed with 0.350 g of NaOH in 10 mL of water. The borane moieties were oxidized with 1.420 g of 30% $H_2O_2$ solution in 20 mL of THF. The oxidation reaction was performed for 3 h at 40 °C. The dispersion was poured into 500 mL of MeOH and filtered. The solids were refluxed in MeOH for 0.5 h before distilling off 30 mL of MeOH. The slurry was filtered, and the polymer was dried in a vacuum oven at 40 °C.

For the preparation of the aminated polyethylene, 0.5 g of poly(ethylene-*co*-1,4-hexadiene) containing 2.8 mol % 1,4-hexadiene was placed in a suspension of 15 mL of dry, $O_2$-free THF in an argon-filled drybox. The polymer was hydroborated by the addition of 3 mL of 0.5 M lithium dimethylborohydride solution and 0.166 g of $(CH_3)_3SiCl$. The polymer slurry was heated to 65 °C for 3 h in a flask equipped with a condenser and then 0.34 g of hydroxyamino-*o*-sulfonic acid was added under $N_2$ at room temperature. After 0.5 h at 0 °C, the reaction was warmed to 40 °C for 12 h before adding 10 mL of water. The polymer was then isolated by precipitation in MeOH. Repeated washing with methanol was performed before drying the resulting polymer under vacuum.

## Conclusion

In this paper, we have shown an effective route to prepare functionalized polyethylene with a broad range of functional groups, such as $BR_2$, OH, $NH_2$, and $OSi(CH_3)_3$, and functional group concentrations. The chemistry involves two steps, including the synthesis of unsaturated PE and subsequent functionalization using borane reagents. The combination of newly developed homogeneous single-site catalyst, $Et(Ind)_2ZrCl_2$/MAO, and 1,4-hexadiene comonomer provides excellent control in both process and product during the copolymerization reaction. A broad range of copolymer compositions with relatively well-defined copolymer structures were obtained. Despite the heterogeneous reaction conditions employed, the hydroboration reactions of unsaturated PE copolymers were highly efficient under relatively mild reaction conditions. With the appropriate borane reagents and the secondary C−B bond formed in the hydroboration reaction, quantitative interconversions from borane groups to other functional groups were observed. Overall, this chemistry not only achieves the functionalization of polyethylene, but also preserves molecular weight, crystallinity, and processibility of polyethylene.

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