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Kinetic Aspects of the Copolymerization between α-Olefins and Borane Monomer in Ziegler–Natta Catalyst

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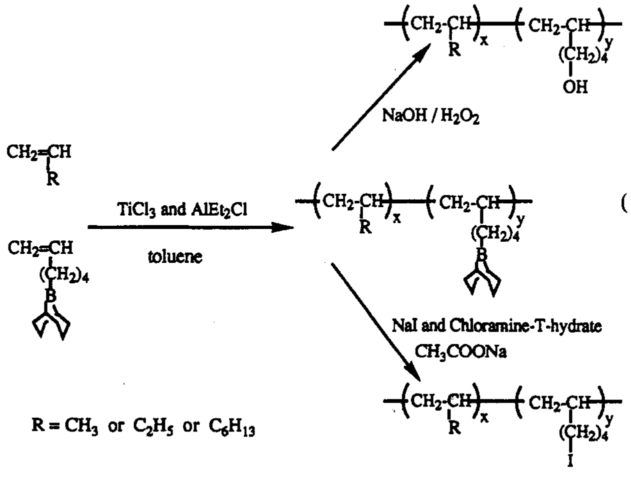
ABSTRACT: This paper focuses on the reactivity of a borane monomer, e.g., 5-hexenyl-9-BBN, in Ziegler–Natta copolymerization with α-olefins, e.g., propylene, 1-butene, and 1-octene. The monomer reactivities were studied by reactivity ratio, copolymer compositions during the reaction and copolymer microstructure. In general, the borane monomer can be effectively incorporated into polyolefins with controllable concentrations and locations. Due to the excellent stability of boranes to the catalyst and solubility of boranes in hydrocarbon solution, the borane monomer behaves as a high α-olefin monomer in Ziegler–Natta polymerization. In turn, the trialkylboranes in copolymers are easily converted to various functional groups under homogeneous or heterogeneous reaction conditions. In the cases of polypropylene and poly(1-butene), the chemistry not only achieves functionalization but also preserves most useful physical properties, such as crystallinity and thermal stability, of the isotactic homopolymers.

Introduction

Functionalization of polyolefins[1,2] has long been a scientific challenge in searching to improve their adhesion to and compatibility with other materials. Only a few chemical processes with very limited success have been demonstrated to functionalize polyolefins. Generally, the modification reactions of highly crystalline polypropylene and poly(1-butene) are accompanied by undesirable side reactions, such as degradation[3] of the polymer backbone and low functional group concentration. Unfortunately, Ziegler–Natta catalysts are normally incapable of incorporating functional group-containing monomers because of catalyst poisoning.[4] It is clear that there is a fundamental need to develop a new chemistry which can address the challenge of preparing functionalized polyolefins, especially polypropylene and poly(1-butene), with controllable molecular weight and functional group concentration.

In the past few years, we have been investigating a new approach to the functionalization of polyolefins by via borane-containing polymers.[5,6] The chemistry has focused on the direct copolymerization of borane monomers[7–9] and α-olefins with Ziegler–Natta catalysts as shown in eq 1.



(1)

The success of the borane approach is due to several facts: (a) The borane group is stable to transition metal catalysts. (b) The borane monomers and polymers are soluble in pure hydrocarbon media. This combination ensures the formation of high molecular weight copolymers with desirable functional group concentrations. In fact, the reaction conditions for α-olefin polymerization can be directly applied in the incorporation of borane monomers. (c) In addition, the borane groups in the copolymers are extremely versatile synthetic intermediates[10–12] and can be effectively transformed to a remarkably fruitful variety of functionalities under mild reaction conditions.

Results and Discussion

In this paper, we will focus on the kinetic aspects of copolymerization reactions by investigating the reactivity ratio of comonomers, incorporation of borane monomers during the reaction, and copolymer microstructures. The systematic study involves the copolymerization between borane monomer (5-hexenyl-9-BBN) and various α-olefins, such as propylene, 1-butene, and 1-octene. In a typical example, the reaction was carried out in an inert gas atmosphere at ambient temperature using $TiCl_3 \cdot {}^1/_3AlCl_3$ and $Al(Et)_2Cl$, a heterogeneous isospecific catalyst. The polymerization was started by the addition of the catalyst mixture, after aging for 0.5 h, to a solution of the two monomers in toluene. The resulting polymer solution was very dependent on the α-olefin used. In the 1-octene case, a homogeneous purple suspension was observed through the whole copolymerization reaction. On the other hand, in the polypropylene case a white precipitate could be seen in the deep purple slurry almost immediately. The precipitation is due to the crystalline structure resulting from highly isotactic propylene sequences. The copolymers were sampled during the reaction, and the copolymerization was terminated after a specified reaction time by addition of 2-propanol to destroy the active metal species. Excess 2-propanol was used to ensure the complete coagulation of any polymer from solution. The borane-containing polymers were isolated from solution by simple filtration and then washed repeatedly with 2-propanol.

The resulting borane-containing copolymers, poly(propylene-*co*-5-hexenyl-9-BBN) and poly(1-butene-*co*-5-hexenyl-9-BBN) containing low concentrations of borane monomers (<10 mol %), are insoluble in common organic solvents at room temperature, but soluble at high temperature. On the other hand, the copolymers of poly(1-

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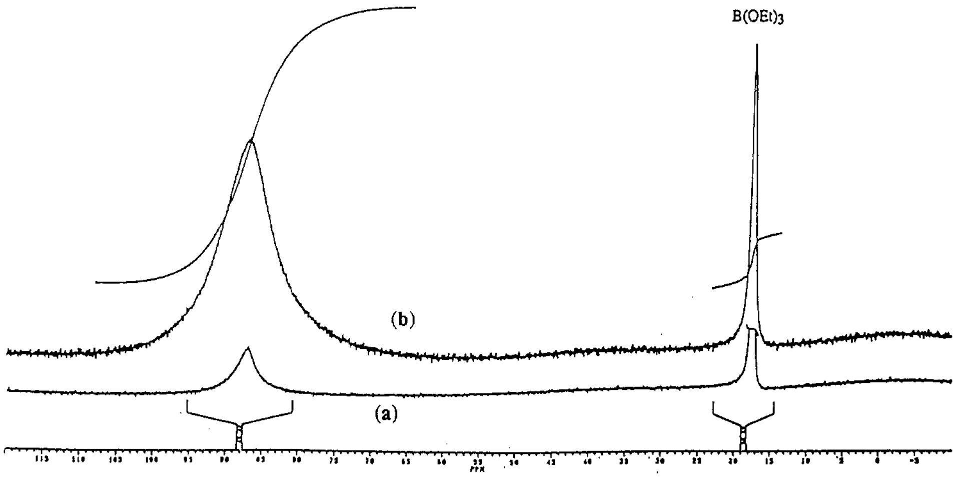

Figure 1. Comparison of ^{11}B NMR spectra between poly(propylene-*co*-hexenyl-9-BBN) with 5% borane mole concentration (a) and 5-hexenyl-9-BBN (b).

Table I. A Summary of Copolymerization of Borane Monomer and α-Olefins in 1-h Batch Reactions

copolymers	mol % B[a] in feed	mol % B[a] in copolymer	% yield
PP-B	10	0.3	66
PP-B	50	3.5	38
PB-B	25	15	64
PB-B	50	37	58
PO-B	25	18	65
PO-B	50	40	55
PO-B	75	62	45

[a] B ∫ 5-hexenyl-9-BBN.

octene-*co*-5-hexenyl-9-BBN), in all compositions, are soluble in hydrocarbon solvents at room temperature. The borane concentration can be measured by solution ^{11}B NMR technique. Only a single chemical shift at 87 ppm (vs $BF_3{\cdot}OEt_2$), corresponding to a trialkylborane, was observed in all copolymers as shown in Figure 1. The same peak exists in both monomer and polymer showing that no detectable side reactions occurred during polymerization and workup. By using a known concentration of triethyl borate (chemical shift at 19 ppm) as a reference and comparing the integrated peak areas, the borane content in the copolymer can be quantitatively determined. The results are in good agreement with those determined by ^1H NMR spectra of the corresponding hydroxylated polymers (discussed later). Table I summarizes the experimental results of poly(propylene-*co*-5-hexenyl-9-BBN) (PP-B), poly(1-butene-*co*-5-hexenyl-9-BBN) (PB-B), and poly(1-octene-*co*-5-hexenyl-9-BBN) (PO-B) prepared under various reaction conditions. The reactivity of the monomers is obviously different, propylene ≫ 1-butene > 1-octene > 5-hexenyl-9-BBN. Basically, the reactivity of 5-hexenyl-9-BBN follows the same trend as high α-olefins in heterogeneous Ziegler–Natta polymerization: the smaller the size the higher the reactivity. The reactivity becomes less disparate with larger α-olefins.

The borane-containing copolymers are stable for long periods of time (6 months in a drybox) or at elevated temperatures (130 °C during NMR measurement) as long as O_2 is excluded. By exposing a copolymer to air, the copolymer becomes insoluble at any temperature. The oxidation of borane groups by oxygen causes a crosslinking reaction due to the generation of polymeric free radicals.[13] In this study, the borane groups in the copolymers were reacted by ionic processes using $NaOH/H_2O_2$ reagents at 40 °C for 6 h. The borane groups were completely converted to the corresponding hydroxy groups even in the heterogeneous PP-B and PB-B cases. The high exposure of the pendant organoboranes may be due to a semicrystalline microstructure (discussed later) of the copolymers. Figure 2a shows the ^1H NMR spectrum of the hydroxylated polypropylene (PP-OH) with 5 mol % hydroxy groups. The peak at 3.5 ppm corresponds to the methylene protons ($-CH_2OH$) on the primary alcohol carbon atom.

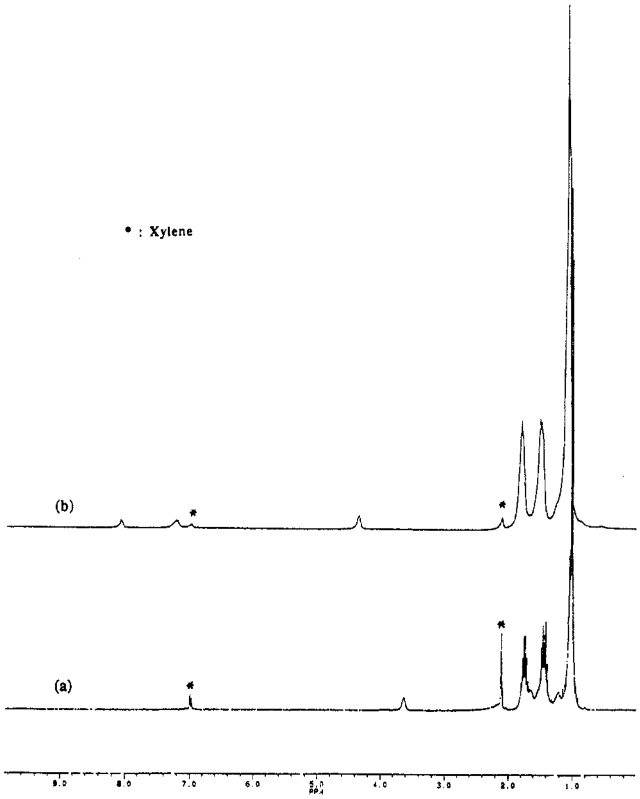

Figure 2. ^1H NMR spectra of the hydroxylated polypropylene with 5 mol % of hydroxy groups (a) and its corresponding esterified form by reacting with benzoyl chloride (b).

The PP-OH polymer can be further modified to its ester form by benzoyl chloride. As shown in Figure 2b, the esterification was complete with the disappearance of the primary alcohol peak at 3.5 ppm and the appearance of $CH_2OC{=}O$ at 4.0 ppm and two aromatic bands around 7.2 and 8.1 ppm. To determine the copolymer compositions, the peak at 3.5 ppm in Figure 2a was integrated with reference to the three (major) overlapping peaks between 1.95 and 0.72 ppm to compare the number of

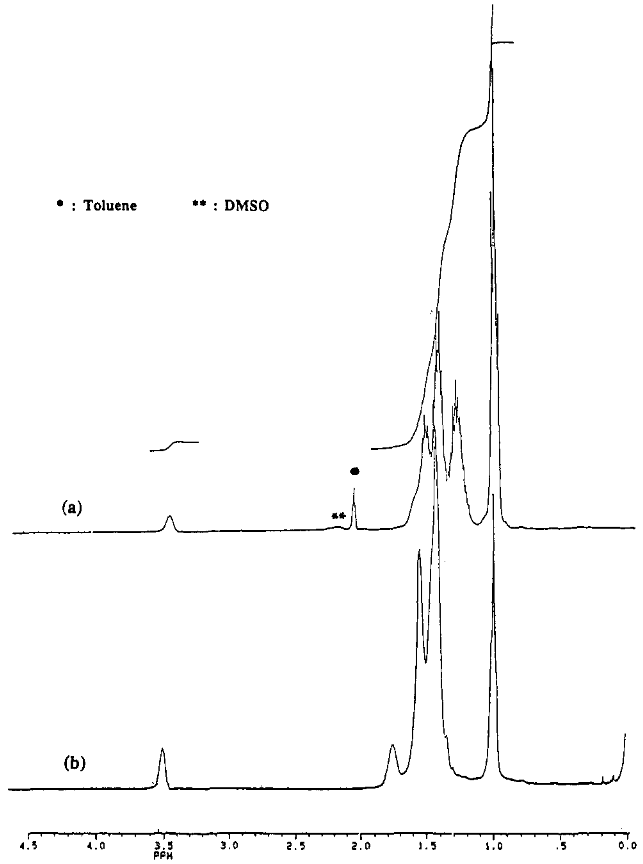

Figure 3. ^{1}H NMR spectra of the hydroxylated poly(1-butene) and poly(1-octene) with 7 mol % (a) and 20 mol % (b) hydroxy groups.

protons adjacent to the alcohol (–CH_2OH) to the rest of the aliphatic protons from the propylene and hexenol repeat units. The same results was also obtained in the corresponding esterified polymer by comparing the peak at 4.0 ppm to the rest of the aliphatic protons in Figure 2b.

Likewise, other olefin copolymers were completely oxidized. Figure 3 shows hydroxylated poly(1-butene) (PB-OH) and poly(1-octene) (PO-OH) with 7 and 20 mol % of hydroxy groups, respectively. Trialkylborane polymers were also converted to the corresponding iodine-containing polymers. Conversion of borane to iodine groups was complete using NaI and chloramine-T hydrate under basic conditions at room temperature. The mild oxidizing agent chloramine-T and iodine source NaI generate I^+ in situ which reacts with the borane base complex by an S_E2 mechanism. The facile conversion is similar to those of small borane molecules[14] and borane-terminated telechelic polymers.[15] The resulting iodine-containing polymers were soluble in hydrocarbon solvents. However, the iodide polypropylene was initially soluble in xylene at 130 °C and soon became yellowish and increasingly less soluble.

Copolymer Compositions vs Reaction Time. The change in copolymer composition during the reaction is a useful way to understand the copolymerization reaction. In a batch reaction, the copolymers were sampled during the copolymerization of α-olefins and 5-hexenyl-9-BBN with a 1:1 monomer feed ratio. Figure 4 shows the plot of 5-hexenyl-9-BBN (mol %) in the copolymers versus reaction time. In the copolymerization of 1-octene and 5-hexenyl-9-BBN, the copolymer compositions are relatively flat and are close to the ideal 50 mol % mark as shown in Figure 4a. Only a small increase in borane content in the copolymer with the increasing conversion suggests a slightly higher reactivity of 1-octene as compared to 5-hexenyl-9-BBN. In the 1-butene case, the fluctuation of copolymer composition is more dramatic, especially in the beginning of copolymerization. The reactivity of 1-butene is significantly higher than that of 5-hexenyl-9-BBN. In fact, the copolymer produced at the very beginning of the reaction contains about 7 mol % 5-hexenyl-9-BBN, as determined by extrapolation of the composition to time = 0 in Figure 4b.

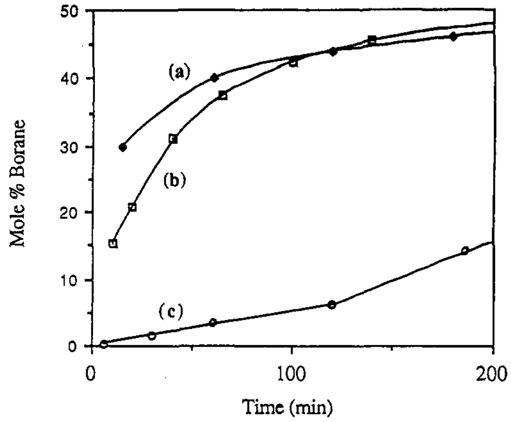

Figure 4. Plots of 5-hexenyl-9-BBN (mol %) in poly(1-octene) (a), poly(1-butene) (b), and polypropylene (c) copolymers versus reaction time.

Table II. Fractionation Results of Hydroxylated Polypropylene (PP-OH) Hot Solvent Soluble Fractions (wt %)

sample	methanol	MEK	heptane	xylene	insoluble
PP-OH A[a]	42.6	18.9	7.6	23.1	7.7
PP-OH B[b]	none	8.5	14.2	77.7	none

[a] Sample (PP-OH-A) was prepared by batch reaction with 1/1 propylene/borane monomer mole ratio. [b] Sample (PP-OH-B) was prepared by continuous reaction with 10/1 propylene/borane monomer mole ratio.

The initial incorporation of borane monomer in the polypropylene copolymer was very small as shown in Figure 4c, only 1.6 mol % in the first 0.1 h, increasing to 3.5 and 6 mol % after 1 and 2 h, respectively. It is obvious that propylene was preferentially polymerized in the initial stages of the copolymerization and was consumed in the feed much more quickly. This has the effect of a monomer feed gradient over time (decreasing % of propylene and increasing % of 5-hexenyl-9-BBN). The constant change in monomer ratio certainly results in a broad copolymer composition. A sample (PP-OH-A) obtained at near complete monomer conversion (16 h reaction time) using a 1/1 monomer feed ratio followed by oxidation was subjected to fractionation by sequential Soxhlet extractions using various solvents. The solvents were chosen so as to separate by polarity (OH content) and crystallinity (isotacticity and PP sequence length). The sample was extracted with methanol, 2-butanone (MEK), heptane, and xylene all under N_2. Table II shows the fractionation results of PP-OH-A which are compared with those of sample PP-OH-B prepared by continuous reaction (discussed later). PP-OH copolymers with above 60% alcohol content are soluble in MeOH. The MEK fraction was rubbery tacky material indicative of low isotacticity. Due to the low boiling point of heptane, its fraction represents polymer with intermediate tacticity or with more (and/or random distribution) hexenol units in it which reduce crystal formation. Xylene should dissolve all the remaining highly isotactic polymer. However, a small portion (7.7%) of polymer was insoluble after this extraction

Table III. Summary of Copolymerization between Borane Monomer and Propylene or 1-Butene at Low Conversion

sample	mol % B[a] in feed	mol % B[a] in polymer	% yield
PP-B	33.33	1.2	15.2
PP-B	50.00	1.7	11.0
PP-B	66.66	2.7	8.2
PB-B	14.29	2.4	9.9
PB-B	25.00	3.8	8.9
PB-B	33.33	7.0	9.4
PB-B	50.00	15.5	6.3

[a] B ≡ 5-hexenyl-9-BBN.

process. Overall, the results of a high conversion batch reaction show a broad range of composition distribution and microstructure in PP-OH-A copolymer.

Reactivity Ratios. The best way to investigate a copolymerization is to measure the reactivity ratio of the comonomers. To obtain meaningful results a series of experiments were carried out by varying monomer feed ratio and comparing the resulting polymer composition at low conversion. Table III compares feed and copolymer compositions at low conversions. The samples (PP-B) and (PB-B) are obtained from the copolymerization of 5-hexenyl-9-BBN/propylene and 5-hexenyl-9-BBN/1-butene, respectively. The large difference in reactivity between propylene and 5-hexenyl-9-BBN significantly increases the difficulties in determining the actual amount of borane groups in copolymers using low 5-hexenyl-9-BBN concentration at low conversion. The reactivity ratio in this case gives a qualitative, rather than quantitative, expression of the monomer reactivities. On the other hand, 1-butene is much closer to 5-hexenyl-9-BBN in reactivity; therefore, reactivity data are more reliable.

The reactivity ratios between α-olefin ($r_1 = k_{11}/k_{12}$) and 5-hexenyl-9-BBN ($r_2 = k_{22}/k_{21}$) are estimated by the Kelen–Tüdos method. The calculation[16] is based on eq 2 where

$$\eta = r_1\xi - r_2/\alpha(1 - \xi) \qquad (2)$$

$$\eta = G/\alpha + F \qquad \xi = F/\alpha + F$$

x = [α-olefin]/[HB] in feed and y = d[α-olefin]/d[HB] mole ratio in polymer, $G = x(y - 1)/y$, $F = x^2/y$, $\alpha = (F_m \times F_M)^{1/2}$, and F_m and F_M are the lowest and highest values of F. Figure 5 shows the plot η versus ξ and the least-squares best fit line. The extrapolation to $\xi = 0$ gives $-r_2/\alpha$ and r_1. We obtain $r_1 = 70.476$, $r_2 = 0.028$, and $r_1r_2 = 1.973$ for propylene/5-hexenyl-9-BBN and r_1 and 7.13, $r_2 = 0.41$, and $r_1r_2 = 2.92$ for 1-butene/5-hexenyl-9-BBN, respectively.

It is clear that both copolymerization reactions are not ideal cases. The values of r_1r_2 are far from unity, and the reactions are favorable for α-olefin incorporation, especially in the copolymerization of propylene and 5-hexenyl-9-BBN. In the batch reaction with a fixed monomer ratio of propylene/5-hexenyl-9-BBN, either a broad distribution of copolymers was obtained using long reaction times or a narrow compositional distribution was obtained using short reaction times, but in extremely low yield.

Continuous Monomer Feed. It is feasible to obtain more uniform copolymer composition by an engineering approach, such as the control of monomer feed ratio during the copolymerization. In the preliminary experiments, the more reactive α-olefin monomer was added gradually in order to keep its concentration constant relative to the borane monomer. The α-olefin was added in decreasing amounts to account for the consumption of borane monomer in the feed (details described in the Experimental Section). This approach can produce copolymer with a much narrower compositional distribution and higher yield of borane monomer than the corresponding one-shot monomer addition in a batch reactor. The experimental results are summarized in Table IV.

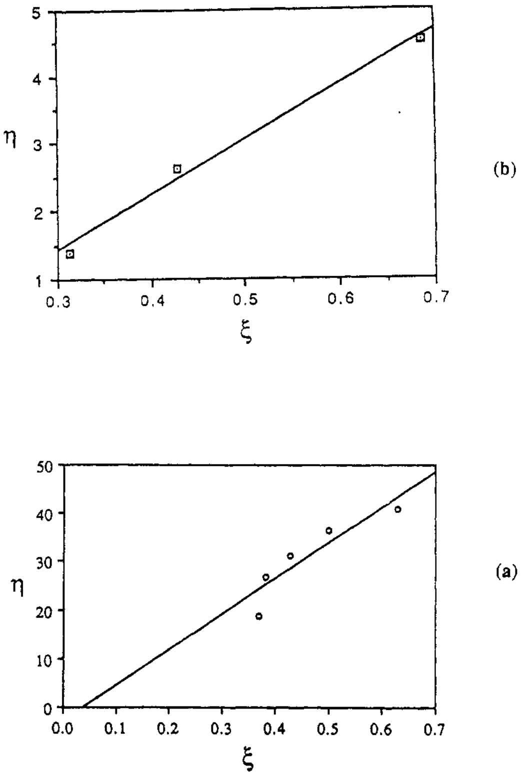

Figure 5. Kelen-Tüdos plots for copolymerization of propylene/5-hexenyl-9-BBN (a) and 1-butene/5-hexenyl-9-BBN (b).

Table IV. Summary of Copolymerization of α-Olefin and Borane Monomer by Continuous Reaction

polymer	mol % B[a] in feed	mol % OH in polymer	reactn time (h)	% yield	η[b]	Mv (g/mol)
PP	0	0	2	93	2.07	230 000
PP-OH	10	3	3	62	1.78	183 000
PP-OH	13	5	5	35	1.71	174 000
PB-OH	5	2.5	2	70		
PB-OH	10	6.5	2	66		

[a] B ≡ 5-hexenyl-9-BBN. [b] η ≡ intrinsic viscosity.

The PP-OH-B prepared from the continuous monomer feed process (total mole ratio of propylene and borane monomer of 10/1) yielded no methanol soluble, 8.5 wt % MEK soluble, 14% heptane, soluble, and 77.2% xylene soluble fractions. Most of PP-OH-B is highly isotactic with a crystalline microstructure.

Molecular Weight. The molecular weights of polymers were determined by intrinsic viscosity measured in a cone/plate viscometer at 135 °C in decalin solution. To enhance the solubility of functionalized polymers, the hydroxylated polymers were completely esterified with benzoyl chloride. Figure 6 shows the viscosity vs concentration for two functionalized polypropylenes and a polypropylene homopolymer, which were prepared under similar reaction conditions. The viscosity average molecular weights (M_v) were calculated using the Mark–Houwink equation

$$[\eta]_0 = K(M_v)^a \qquad (3)$$

where K is 11.0×10^{-3} (mL/g)[17] and a is 0.80. As shown in Table IV, M_v's are high, about 200 000 g/mol, for all samples. The lack of significant change in the molecular weight due to the addition of the borane monomer is quiet interesting, especially under heterogeneous reaction con-

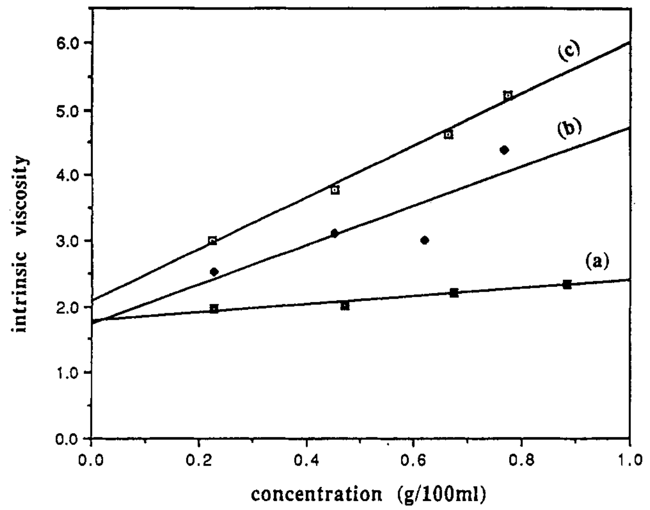

Figure 6. Plots of viscosity vs concentration for two esterified polypropylene copolymers containing 3 mol % (a) and 5 mol % (b) ester groups and a polypropylene homopolymer (c).

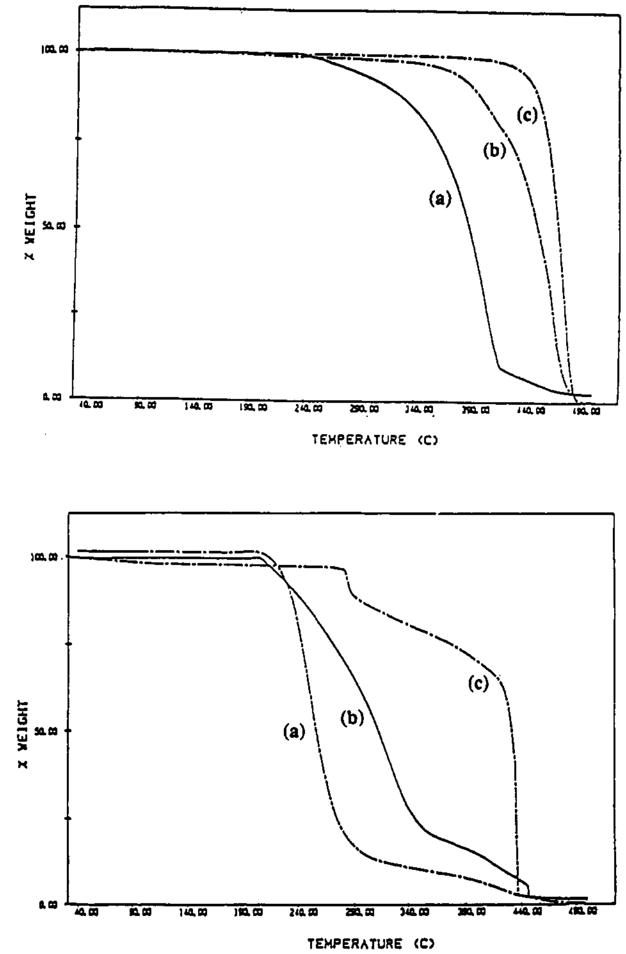

Figure 7. TGA curves of isotactic polypropylene (a), poly(propylene-*co*-hexen-6-ol) with 5 mol % alcohol groups (b), and polyhexen-6-ol (c) in air (bottom) and under argon (top).

ditions. No catalyst poisoning by the borane groups is indicated. In addition, the solubility of the borane group offers the same reaction conditions as an α-olefin in homopolymerization.

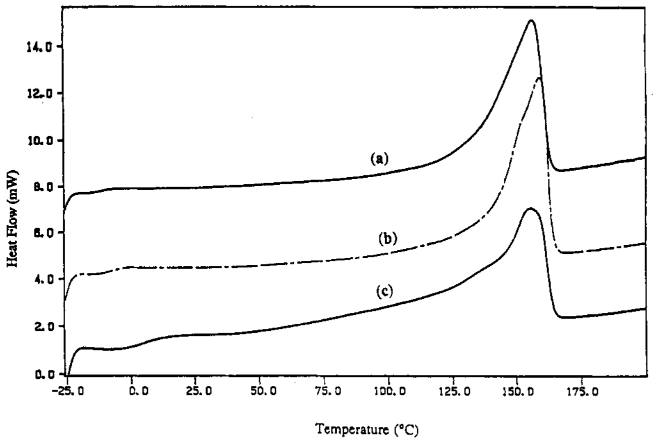

Figure 8. Comparison of DSC curves between isotactic polypropylene (a) and poly(propylene-*co*-hexen-6-ol) with 1 mol % (b) and 5 mol % (c) alcohol groups.

Thermal Stability. Thermal stability is certainly a very important aspect in the functionalization of polymers. The preservation of thermal stability is desirable for processing the polymers. Figure 7 compares the TGA results between PP-OH copolymer with 5 mol % hydroxy groups and two homopolymers, isotactic PP and polyhexenol, under argon and air atmospheres. The thermal stability of PP-OH is higher than that of pure isotactic polypropylene. The decomposition temperature of hydroxy polypropylene is above 280 °C in argon and about 205 °C in air. A slightly better resistance in decomposition may be contributed from the relatively high thermal stability of polyhexenol. This thermal stability stems from the excellent stability of the primary alcohol and the fact that the functional group is pendant on a side chain. These advantages are illustrated by comparison to poly(vinyl alcohol) which thermally decomposes below 150 °C. Primary alcohols are more thermally stable than secondary alcohols. In addition, the decomposition of functional groups in the pendent side chains will not affect the polymer backbone, and the copolymer will maintain its high molecular weight and mechanical properties.

Crystallinity Studies. Both DSC and polarized optical microscopy were used to study the crystallinity of copolymers. Figure 8 shows the comparison of DSC curves of polypropylene homopolymer and hydroxylated polypropylene copolymers obtained from continuous monomer feed. Similar sample weights were used and were treated under the same thermal conditions. All samples have similar melting points (~160 °C) despite the difference in concentration of hydroxy groups. Only a slight shoulder in the PP-OH with the 5 mol % hydroxy groups sample was observed, indicating the existence of lower melting, smaller crystalline phases.

The crystalline structure of functionalized polypropylene was also studied by polarized optical microscopy. As shown in Figure 9, the same PP-OH copolymers with 5 mol % hydroxy groups was compared with isotactic polypropylene. Both samples were treated under the same thermal conditions. The trend is consistent with DSC results. Both micrographs clearly show the typical i-PP spherulites with high overall crystallinity. It is not unusual to see some large spherulites in pure isotactic PP. The spherulites in branched PP-OH are smaller and are more homogeneous in size.

Results in copolymerization reactivity, oxidation reaction, and crystallinity studies imply a semicrystalline microstructure in PP-OH copolymer. The significant difference in comonomer reactivities leads to the preferred incorporation of propylene. The long sequences of propylene units in the polymer backbone form crystalline phases similar to those in pure isotactic polypropylene. While the polypropylene segment can crystallize, the borane groups located at the end of side chains are expelled out of the crystalline phase into the amorphous region.

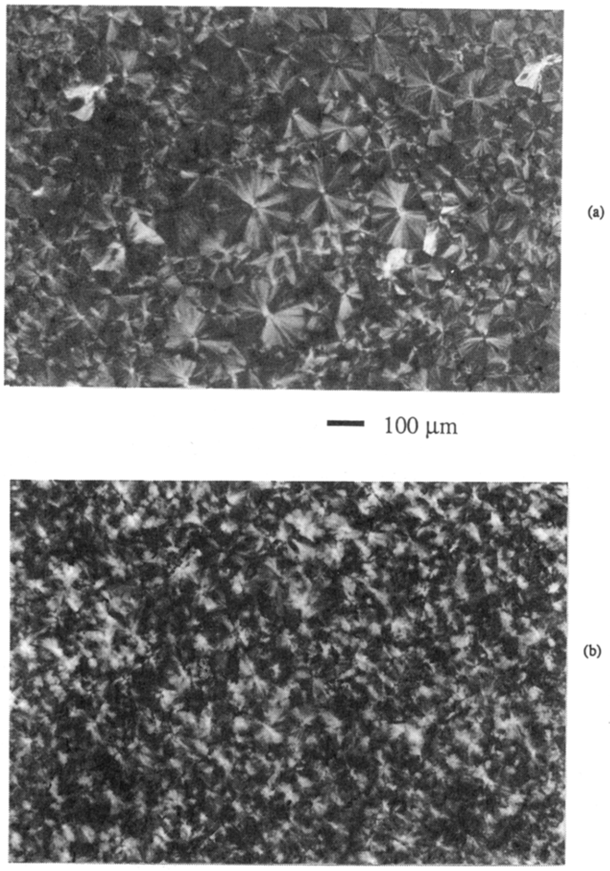

Figure 9. Comparison of optical micrographs between isotactic polypropylene (a) and poly(propylene-*co*-hexen-6-ol) with 5 mol % alcohol groups (b).

The high exposure and mobility of the pendant organoborane groups offer the conditions for complete chemical conversions to various functional groups. It is remarkable to note that the reactions were performed in a heterogeneous medium, involving a crystalling, hydrophobic polyolefin and an aqueous reagent, under mild reaction conditions.

Effective preservation of crystallinity and thermostability in the functionalized polypropylene is very important. The PP-OH copolymers can be processed to form various shapes and sizes under the same conditions used for isotactic polypropylene. In addition, the PP-OH copolymer can cocrystallize with pure isotactic polypropylene in polymer blends. Also, PP-OH is an effective surface modifier[18] to improve PP adhesion to other materials, such as aluminum and glass.

Experimental Section

Instrumentation and Materials. All room- and high-temperature ^{1}H NMR, ^{13}C NMR, and ^{11}B NMR were recorded on a Bruker WP-200 or a Bruker AM-300 spectrometer with the DISNMR software. Quartz NMR tubes were used in ^{11}B NMR measurements. Fourier transform infrared spectroscopy was performed on a Digilab FTS-60 instrument on solution cast films on KBr windows. Pressed KBr pellets were analyzed on a MB-100 Bomem spectrometer. Differential scanning calorimetry (DSC) was measured on a Perkin Elmer DSC-7, TAC-7 instrument controller. The DSC's were measured from −30 to 200 °C with a heating rate of 20 °C/min. Thermogravimetric analysis was accomplished using the Perkin-Elmer TCS-2 thermogravimetric analyzer. Weight loss versus temperature was measured under argon and under a 30/70 O_2 and argon mixture with a heating rate of 10 °C/min. All O_2- and moisture-sensitive manipulations were performed inside an argon-filled Vacuum Atmosphere drybox equipped with a MO-40-1 dry-train.

For optical microscopy studies, polymer solutions were prepared in BHT-inhibited xylene at 135 °C. The polymer films were then solution cast onto glass microscope slides. After the xylene was evaporated under N_2 purge, the films were covered with a slide cover. The polymer films were then melted in a hot stage at 180 °C for 15 min. The samples were then allowed to cool quiescently in the hot stage to room temperature for 20 min. The magnification on the microscope was 100 times. Viscosity measurements were taken using a cone/plate rotational Brookfield digital viscometer Model DVII. The viscosity of polymer solutions in decahydronaphthalene (decalin) inhibited with BHT were determined at 135 °C. The alcohol-containing copolymers were esterified before their viscosity was measured. Solutions of the copolymers in dry xylene and pyridine were esterified by benzoyl chloride to their respective benzoic ester copolymers to improve their solubility in decalin.

HPLC-grade tetrahydrofuran and toluene were deoxygenated by argon sparge before being refluxed for 48 h and then distilled from their respective green or purple sodium anthracide solution under argon. 2-Propanol was refluxed in CaH_2 before being distilled under argon. All three solvents were stored in the drybox. 2-Propanol was kept in the drybox's freezer to reduce vapor pressure. 1,5-Hexadiene obtained from Aldrich was dried over CaH_2 and then distilled under vacuum prior to use. 9-Borabicyclononane (9-BBN), diethylaluminum chloride, chloramine-T hydrate, and sodium iodide were used as received from Aldrich. The titanium trichloride ($TiCl_3$·AA) which was aluminum reduced and activated was used as received from Stauffer Chemicals. Propylene from Metheson and 1-butene from Aldrich were passed through molecular sieves, phosphorous pentoxide, and sodium hydroxide drying columns before being condensed into a graduated Schlenck flask containing triethylaluminum before using. The borane monomer, such as 5-hexenyl-9-BBN, was prepared by the published method.[7]

Copolymerization of Propylene and Hexenyl-9-BBN in Batch Reaction. In a typical copolymerization, 15.5 mL (10.09 g, 0.2401 mol) of dried propylene liquid at −78 °C was transferred into a 500-mL Schlenk flask containing 200 mL of degassed frozen toluene. This reaction flask was then warmed to room temperature before being brought into the drybox where 49.03 g (0.2401 mol) of hexenyl-9-BBN was added via the side-arm bulb. Note that the reactor contains a negative pressure. The residual monomer was washed in with 10 mL of toluene.

Meanwhile, 4.093 g (5.585×10^{-2} mol) of $AlEt_2Cl$ in 15 mL of toluene was added dropwise to the burgundy slurry of 15 mL of toluene and 0.901 g (5.97×10^{-3} mol) of solid $TiCl_3$AA. This catalyst was premixed for 0.5 h before being added to the reactor via the side-arm bulb. After 2 h of polymerizing at room temperature, cold 2-propanol (20 mL) was added to terminate the polymerization as shown by the color change from deep burgundy to clear, pale brown. The reactor contents were then poured into a bottle containing 300 mL of 2-propanol. The bottle was sealed and placed in the drybox freezer overnight to facilitate the polymer precipitation or coagulation (depending on the borane content). The polymer was isolated by filtration, washed with more 2-propanol, and squeeze dried, all in the drybox. A small amount of white rubbery polymer was vacuum dried, dissolved in *o*-xylene-d_{10}, and analyzed by ^{11}B-NMR at 120 °C using triethyl borate as a standard.

Copolymerization of Propylene and Hexenyl-9-BBN in Continuous Reaction. In an argon-filled drybox, 15.477 g of 5-hexenyl-9-BBN and 200 mL of hexane were placed in a a Parr 450-mL stirred pressure reactor and sealed. Outside the box, 4.6 g of propylene was added under N_2 pressure. A slurry of 1.027 g of $TiCl_3$·AA and 4.705 g of $AlEt_2Cl$ in 80 mL of toluene was then added under N_2 pressure to catalyze the copolymerization. Additional propylene was added at 30-min intervals with 4.10, 3.60, 3.20, 2.80, and 2.00 g of propylene added, respectively. After the last monomer charge, the reaction was performed for an additional hour before being terminated by injection of 100 mL of 2-propanol. The reaction was stirred for an additional 0.5 h before the excess pressure was vented and taken into the box for further purification with IPA.

Oxidation and Iodozation Reactions. The polyborane was placed in a 2000-mL round-bottom flask equipped with septum and stirrer in 700 mL of THF to form an inhomogeneous slurry.

A solution of 19 g of NaOH in 60 mL of water, 30 mL of THF, and 20 mL MeOH was degassed and added dropwise into the reactor. The flask was then cooled to 0 °C before a degassed solution of 87.6 g of 30% aqueous H_2O_2 in 75 mL of THF was slowly added via a double-tipped needle. The reaction was allowed to slowly warm to room temperature before being heated to 40 °C for 6 h. The hydroxylated polymer was then precipitated in water, squeeze dried, and placed in a slurry of 500 mL of methanol. After 3 h of vigorous stirring, approximately 75 mL of MeOH was distilled under N_2 to remove boric acid–methanol azeotrope. Again the polymer was precipitated in water, squeeze dried, washed with acetone, and dried under high vacuum at 45 °C.

For the iodozation reaction, 0.231 g of white powdery of PP-B copolymer was placed in a suspension of THF in a 150-mL round-bottom flask equipped with a magnetic stir bar and a rubber septum. A degassed solution of 0.012 g of sodium acetate in 10 mL of methanol was added via a syringe under N_2. This was followed by the dropwise addition of 0.020 g of NaI in 5 mL of degassed water. The cloudy white polymer suspension turned pale yellow and faded after 0.016 g of chloramine-T hydrate in 10 mL of degassed MeOH was added. After 2 h of stirring at room temperature the reaction was terminated by addition of aqueous sodium thiosulfate followed by 300 mL of dilute HCl to precipitate the polymers. The polymer was repeatedly washed with water and acetone. The solid was placed in a refluxing MeOH slurry and precipitated in water two times before drying under vacuum. The infrared spectrum was analyzed for a KBr pellet of the white plastic.

Conclusion

In this paper, we have shown the copolymerization reaction of borane monomer and α-olefins, e.g., propylene, 1-butene, and 1-octene, using Ziegler–Natta catalysts. The reactivity of borane monomer follows the same trend found in all α-olefins, that is the smaller the size of the α-olefin the higher its reactivity while the reactivity becomes less diparate in higher α-olefins. The stability of the borane groups to Ziegler–Natta catalysts, their solubility in hydrocarbons, and their synthetic versatility in being convertible to various functional groups offer a general method in the functionalization of polyolefins. A range of functionalized polyolefins have been obtained with high molecular weights and controllable functional group concentrations and microstructures. In the cases of polypropylene and poly(1-butene), the chemistry not only achieves functionalization but also preserves the desirable physical properties, e.g., crystallinity and thermal stability, of the isotactic homopolymers. The combination of functional groups on the side chains and isotactic polyolefin sequences results in unique morphological arrangement, in which the polymer crystallizes but functional groups are concentrated in the amorphous region. This type of copolymer has been demonstrated as a very effective interfacial modifier[18] for improving adhesion between polyolefins and substrates. In addition, the copolymer is a very promising support material[19] for immobilized catalysts.

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