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# Articles

## Synthesis of Polyalcohols via Ziegler–Natta Polymerization

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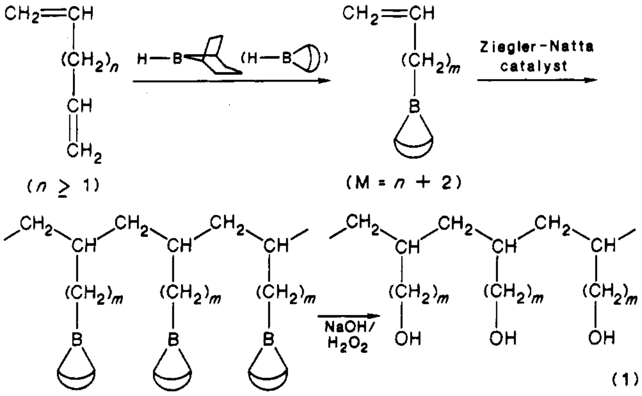
ABSTRACT: Functional polymers are normally difficult to prepare by Ziegler–Natta polymerization because of catalyst poisoning and other side reactions. This paper describes the synthesis of functional α-olefins via the intermediacy of novel borane monomers and polymers. Borane monomers, derived from monohydroboration of appropriate dienes with dialkylborane, have been found to be stable to titanium-based Ziegler–Natta catalysts. In turn, the borane polymers are easily converted to a variety of other functionalities, under mild reaction condition. This paper will focus on the preparation and molecular structure characterization of polyalcohols prepared according to this route. Moreover, some physical properties, such as high-temperature stability of these materials, will be mentioned in this content.

### Introduction

Incorporation of functional groups into hydrocarbon polymer backbones represents a useful method for modifying the chemical and physical properties of polymers, e.g., permeability, compatibility, dyeability, adhesion, solid-state morphology, and solution rheology. However, functional polymers are normally difficult to prepare by direct Ziegler–Natta polymerization because of catalyst poisoning and other side reactions. The Lewis acid components (Ti and Al) of this catalyst will tend to complex with the nonbonded electron pairs on N and O of functional monomers, in preference to complexation with the π electrons of the double bonds. The net result is the deactivation of the active polymerization sites by formation of stable complexes between catalysts and functional groups. Thus, polymerization is inhibited.

There are some reports of copolymerization of functional monomers with other α-olefins by pretreating functional monomers with a protecting group, such as organoaluminum[1] compound to prevent catalyst poisoning during polymerization. Ester copolymers[2] are especially useful because they are relatively stable to such polymerization and easily converted to acid functionality after polymerization. However, the levels of ester functional group incorporation by such methods remain low, i.e., <5 mol %. The incorporation of high levels of ester functionality requires even more sterically hindered ester monomers, such as 2,6-diphenylphenyl 10-undecanoate.[3] However, the reaction conditions for such a process are very inconvenient (i.e., 65 °C and 10 days). Moreover, the ester polymer is not a versatile intermediate. It is difficult to convert the ester functional polymers to other functional (e.g., –OH, $-NH_2$) polymers by simple mild chemical reactions.

In this paper we describe a new approach, using the intermediacy of novel borane monomers and polymers, to prepare a series of polyalcohol homopolymers. The hydroxyl functional group is separated from the polymer backbone by a flexible carbon–hydrogen spacer group of predesigned length. As shown in eq 1, a borane functionalized α-olefin is obtained from monohydroboration of an appropriate diene with a dialkylborane such as 9-borabicyclo[3.3.1]nonane (9-BBN). Since a borane is a Lewis acid and is stable to titanium- and aluminum-based Ziegler–Natta catalysts, the borane monomer can be polymerized to a borane homopolymer without any precomplex procedure. Consequently, the organoboranes can be transformed to a remarkably fruitful variety of functionalities, e.g., alcohols, acid, amines, etc., as shown by H. C. Brown.[4] In this paper we will focus on the synthesis and characterization of polyalcohols, especially polyoctenol. Its synthesis and characterization will be discussed.



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### Results and Discussion

**Monomers Synthesis.** Nonconjugated terminal dienes, such as 1,7-octadiene, 1,5-hexadiene, and 1,4-pentadiene, were monohydroborated by 9-BBN in THF solution.[5] The major difficulty in achieving the monohydroboration product is the uncontrollable reaction to form dihydro-

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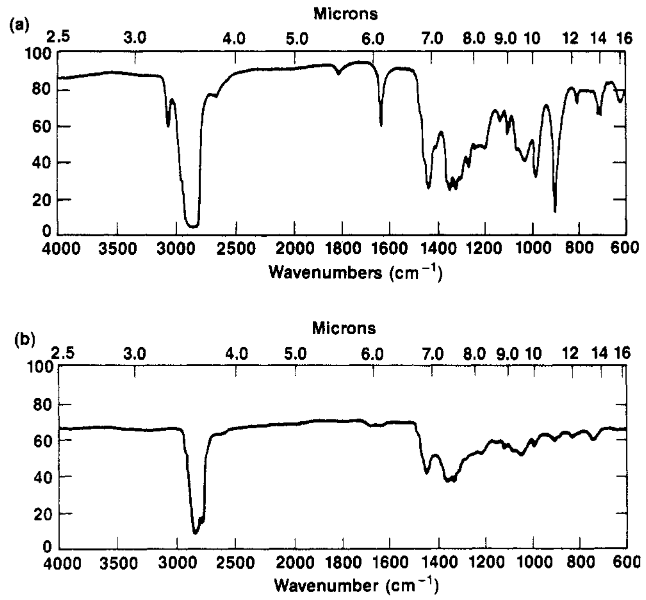

**Figure 1.** IR spectra of *B*-7-octenyl-9-BBN (a) and poly(*B*-7-octentyl-9-BBN) (b).

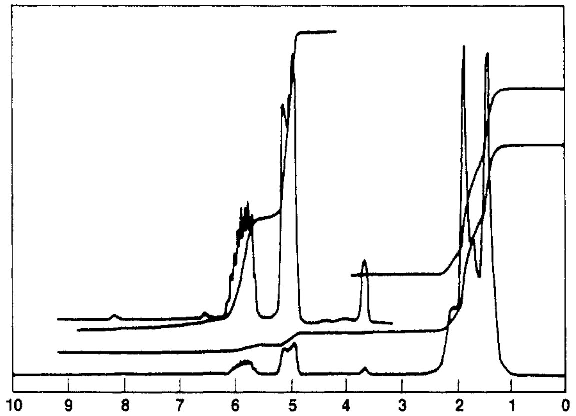

**Figure 2.** $^1$H NMR spectrum of *B*-octenyl-9-BBN in CDCl$_3$.

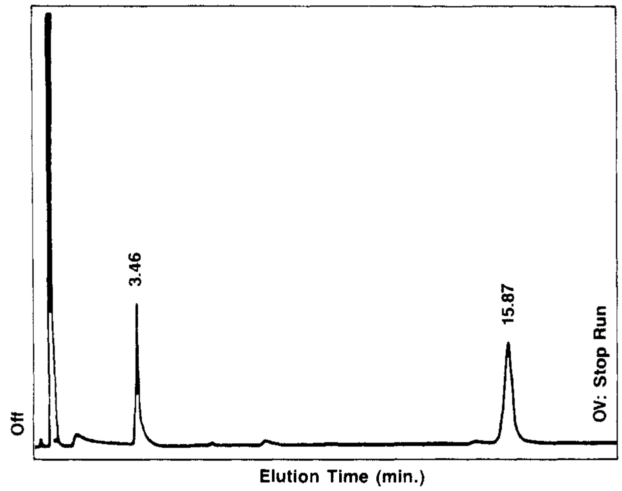

**Figure 3.** GC spectrum of 1-hexanol and 1,5-cyclooctanediol mixture which was obtained from oxidation of *B*-hexyl-9-BBN.

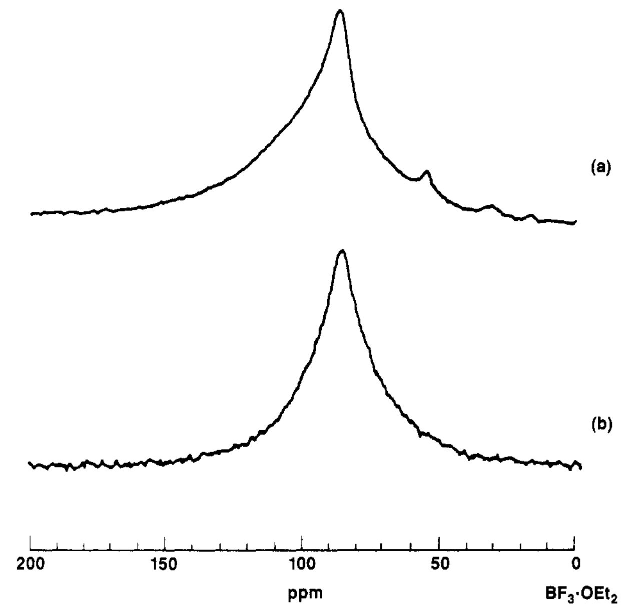

**Figure 4.** $^{11}$B NMR spectra of (a) monomer *B*-7-octenyl-9-BBN and (b) polymer poly(*B*-7-octenyl-9-BBN).

boration product. To optimize the reaction condition, a large excess of diene was used and reaction was carried out at room temperature. After sufficient time for complete reaction, the pure *B*-alkenyl-9-BBN monomer was isolated from the reaction mixture. An IR spectrum of *B*-7-octenyl-9-BBN is shown in Figure 1a; peaks at 3070, 1637, and 905 cm$^{-1}$ characterize the presence of the vinyl group. The $^1$H NMR spectrum in Figure 2 quantitatively shows the exact molar ratio of vinyl protons as expected for monohydroboration of octadiene. Likewise *B*-5-hexenyl-9-BBN and *B*-4-pentenyl-9-BBN were also obtained in the same manner. However, this is not the case in butadiene;[6] the poor reaction yield may be due to the high stability of the conjugated diene.

**Stability of Organoboranes to Ziegler–Natta Catalyst.** The feasibility of polymerizing alkenylboranes by Ziegler–Natta catalysts can be deduced from the stability of such catalysts in organoborane solutions. Since the acidity of *B*-alkenyl-9-BBN is soft, very low reactivity was expected between *B*-alkenyl-9-BBN and Ziegler–Natta catalyst.

A model reaction was examined by mixing *B*-hexyl-9-BBN with stoichiometric amount of TiCl$_3$·AA–Al(Et)$_2$Cl in toluene. The solution was then stirred at room temperature overnight. No visible reaction was observed. The *B*-hexyl-9-BBN was recovered by distillation. A similar $^{11}$B chemical shift (88 ppm vs. BF$_3$·OEt$_2$) was observed in both original and recovered materials. Both trialkylboranes can be oxidized to alcohols as shown by H. C. Brown.[7] The GC result is shown in Figure 3: two GC peaks, one ($t$ = 3.46 s) for 1-hexanol and a second one ($t$ = 15.87 s) for 1,5-cyclooctanediol. All results imply that no significant reaction takes place in mixing organoborane and the Ziegler–Natta catalyst. It also suggested to us that borane-substituted $\alpha$-olefins may be polymerized by Ziegler–Natta catalysts and that polyborane polymers may be converted to polyalcohols.

**Polyborane Synthesis.** On the basis of stability tests between trialkylborane and Z–N catalysts, the polymerizability of a series of *B*-alkenyl-9-BBN was examined. A typical monomer of *B*-7-octenyl-9BBN was mixed with a catalytic amount of TiCl$_3$·AA–Al(Et)$_2$Cl/toluene solution in the same manner described in the above model reaction. A viscous polymer solution was observed within a half hour, and then it turned to gel after 2 h. The polymerization was finally terminated, and the polymer was precipitated from the solution by adding pure 2-propanol. A precaution was taken in the purification procedure to prevent an oxidation reaction occurring in the polyborane by air. After all impurities were removed, the polymer was dried under vacuum at 50 °C overnight. A white rubbery material was obtained in 92% yield. The sample was

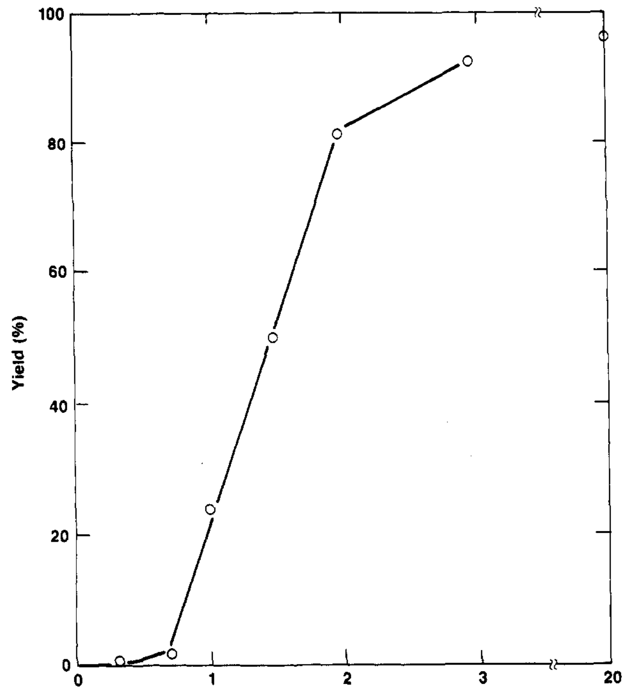

Figure 5. Polymerization yield of poly(7-octenyl-9-BBN) in various reaction time.

**Table I**
**A Summary of Polymerization Yields of Polyboranes**

| Polyborane | Spacer C# | Reaction Time (hr) | Yield | Reaction Mixture | Polymer Form |
|---|---|---|---|---|---|
| poly-7-octenyl-9-BBN | 6 | 3 | 92% | viscous gel | rubbery |
| poly-5-hexenyl-9-BBN | 4 | 2 | 94% | viscous gel | rubbery |
| poly-4-pentenyl-9-BBN | 3 | 6 | 50% | low viscosity | powder |

converted to polyester for GPC measurement. The weight-average molecular weight was above a million.

Infrared spectra of poly(*B*-7-octenyl-9-BBN) were obtained from films cast on KBr windows. The preparation was done in an inert atmosphere. After the solvent was removed, the resulting polymer film was evacuated at room temperature for 2 h to remove the last traces of toluene. An air-tight IR cell was assembled to prevent air diffusion. Infrared spectra of the resulting polymer are shown in Figure 1b. A comparison with that of the monomer in Figure 1a shows that all characteristic vibrational bands for C–C and C–H in the saturated polymer backbone and side chain are similar, with no detectable unsaturated C═C in the polymer. Elementary analysis supports the molecular structure as poly(*B*-7-octenyl-9-BBN) with a C:H:B atom ratio of 16:29:1.

The $^{11}$B NMR spectrum of the polyborane is shown in Figure 4b, a singlet chemical shift a 88.2 ppm (relative to $BF_3$·$OEt_2$), the same as that of the monomer and trialkylborane.[7] The coexistence of the same trialkylborane in both monomer and polymer is crucial, which strongly supports two central points: the stability and polymerizability of an alkenylborane with Ziegler–Natta catalysts. Moreover, the polyborane was also found to be stable to some organic functional groups, such as the alcohol used during the workup procedure. However, it should be remembered that polyboranes are poly Lewis acids and, consequently, are very reactive under certain conditions. In air, the oxidation reaction proceeded rapidly to produce alkyl borinate.

**Kinetic Studies of Polymerization.** In order to understand the polymerization reactivity in detail, a series of kinetic runs were carried out by precipitating the polymer from the reaction solution after a particular period of reaction time. This method is suitable for high molecular weight polymers that can be quantitatively precipitated by adding polar materials in which the polymer is insoluable. The result is shown in Figure 5. After an induction period, the amount of poly(7-octenyl-9-BBN) formed was proportional to reaction time. The polymerization was almost complete after 3-h reaction time with more than 90% yield.

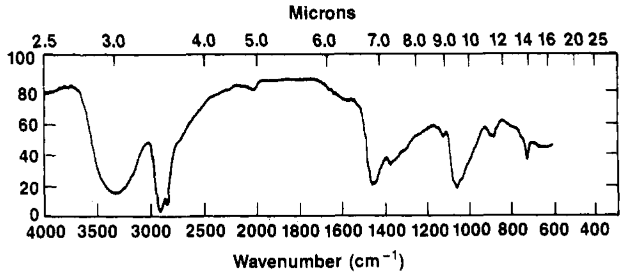

Figure 6. IR spectrum of polyocten-8-ol.

**Table II**
**Elemental Analysis Results of Polyoctenol**

| $(C_8H_{16}O)_x$ | C | H | O | B | Total (%) |
|---|---|---|---|---|---|
| Theoretical Values | 75.0 | 12.5 | 12.5 | 0 | 100 |
| Experimental Values | 74.33 | 13.03 | 12.61 | 0.049 | 100.02 |

**Table III**
**Characteristics of the Infrared Spectrum of Polyoctenol**

| Frequency (cm$^{-1}$) | Relative Intensity | Assignment |
|---|---|---|
| 3300 | Strong | O-H Stretching |
| 2900 | Strong | C-H Stretching |
| 2840 | Strong | C-H Stretching |
| 1440 | Strong | C-H and O-H Bending |
| 1370 | Medium | $CH_2$ Wagging |
| 1050 | Strong | C-O Stretching |
| 720 | Medium | $Ch_2$ Rocking |

A slightly higher reactivity was observed when 5-hexenyl-9-BBN was used. As shown in Table I, a quantitative amount of poly(5-hexenyl-9-BBN) was obtained within 2 h. In contrast, a dramatic decrease in reactivity occurred when the polymerization of 4-pentenyl-9-BBN was attempted. Under the same reaction conditions, no visible change in reaction solution was observed. A fine powder was isolated after adding polar solvent. On the basis of this information, it suggests that the polymerization reactivity appears to increase with a decrease of space group between double bond and borane moiety. However, it is necessary to insulate the double bond from a borane moiety. A space with more than three methylene units is needed to minimize the electron-withdrawing effect which decreases the electron density in double bond. Similar results were found in other studies using functional monomers containing ester[1,8] or amine[9] functions.

**Polyalcohol Synthesis.** As will be shown in the Experimental Section, polyboranes are easily oxidized to polyalcohols under mild conditions. For example, poly(*B*-7-octenyl-9-BBN) was reacted with sodium hydroxide and hydrogen peroxide at 50 °C for 2 h to produce pure polyocten-8-ol homopolymer. Elementary analysis (shown in Table II) was in good agreement with the theoretical value and confirmed that quantitative conversion was obtained as in the case of small size of organoboranes. It is important to note that polyboranes are poly Lewis acids and very soluble in hydrocarbon solvents. Those high reactivities and solubilities of polyboranes give us the best

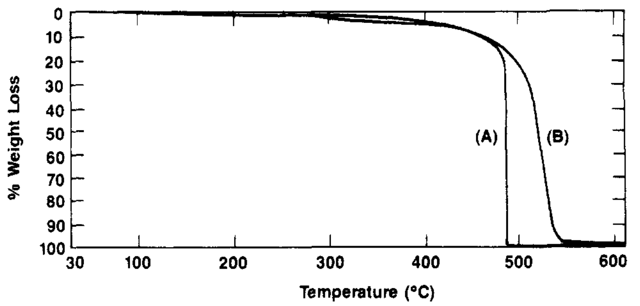

**Figure 7.** Thermogravimetric analysis curves of polyocten-8-ol (heating rate = 10 °C/min). Atmosphere: (A) flowing $O_2$; (B) flowing Ar.

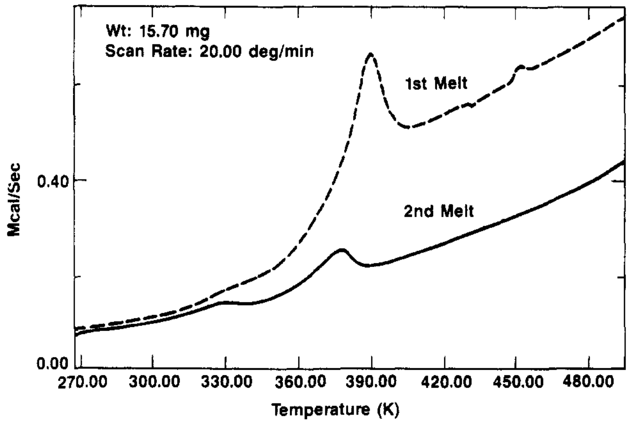

**Figure 8.** DSC results of polyocten-8-ol.

opportunity to use polyboranes as intermediates to synthesize other functionalized polymers, such as polyamines, polyaldehydes, polycarboxylic acids, etc. Those homo- and copolymers will be discussed in future papers.

**Spectral and Physical Properties of Polyalcohols.** Many polyalcohols with various numbers of methylene groups have been synthesized and characterized. However, in the following characterization section we will focus on polyocten-8-ol.

The IR spectrum of polyocten-8-ol was obtained from a film of polyocten-8-ol of thickness 5–10 μm. A uniform film of polyoctenol was formed by the slow evaporation of 1-propanol from a thin layer of polymer solution on a KBr window. The infrared spectrum of polyoctenol, shown in Figure 6 and summarized in Table II, was relatively simple compared to that for poly(vinyl alcohol). The infrared absorption bands of poly(vinyl alcohol)[10] are all quite broad and overlap severely in the fingerprint region between 1500 and 600 $cm^{-1}$. The reason for this is the difference in symmetry between poly(vinyl alcohol) molecules in the crystalline and glassy states, which contribute two sets of frequencies to the infrared spectrum. However, polyoctenol has relatively well-defined absorption peaks in the same region, which may imply a more symmetrical molecular structure in the polymer matrix. It may also be due to isotactic propagation during polymerization. The resulting high degree of ordering of the inside groups was also observed in an X-ray pattern that will be discussed later.

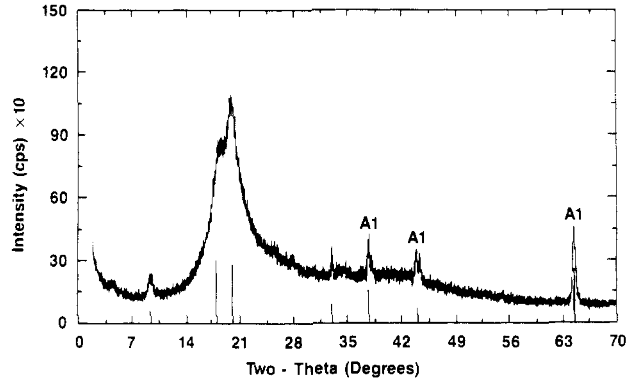

**Figure 9.** X-ray diffraction of polyocten-8-ol.

The thermogravimetric analysis results of the polymer powder are shown in Figure 7. In an inert atmosphere (e.g., Ar), the polymer powder exhibits surprisingly high thermal stability; less than 3% weight loss was observed at 300 °C. The decomposition took place above 400 °C and rapidly increased over 500 °C. The good thermal stability of polyocten-8-ol is quite different from that of poly(vinyl alcohol) which is dehydrated at about 170 °C and further decomposed above 250 °C.[10] These results obviously suggest that the primary alcohol in polyocten-8-ol is more stable than the secondary alcohol in poly(vinyl alcohol). Moreover, the spacing between the hydroxyl group and polymer backbone also impedes decomposition, such as noncatalyzed reverse aldol condensation, which occurs in poly(vinyl alcohol).

In the presence of air, the polymer is stable up to 280 °C, at which point it experiences a minor weight loss. Rapid oxidation took place around 480 °C, resulting in a large weight loss. At 487 °C, the weight loss was nearly complete; most of the polymer was decomposed in air with very little inorganic impurities left. This in good agreement with the elemental analysis result; i.e., the sum of carbon, hydrogen, and oxygen was nearly 100%.

The DSC curve is shown in Figure 8 for polyocten-8-ol. The first deflection at 57 °C corresponds to the $T_g$, and the sharp endotherm peak at 110 °C is assigned to the melting point. After the sample was cooled, the DSC was rerun immediately and showed a relative broad peak. There was no weight loss during the heating cycle. In order to explain those results, one must consider that some crystallinity was formed in polyoctenol, and the crystallinity recovered slowly after the first melt.

The partial crystallinity of polyoctenol was reconfirmed by an X-ray pattern on an unoriented polymer film. As shown in Figure 9, two strong reflections at Brogg angle $2\theta = 18°$ and $20°$ corresponding to spacing ($d'$) of 4.8 and 4.4 Å and one weak reflection at $2\theta = 9.4°$ corresponding to spacing ($d''$) of 9.4 Å were observed. Two reflections at $d' = 4.8$ and 4.4 Å represent the spacing between parallel side chains, analogous to the reflection maximum on X-ray patterns of amorphous $n$-paraffins[11] and polyolefins with long side chains, such as polydecene.[12] The $d'$ values of comblike polymers are quite insensitive to the length of the side chain and fall between 4 and 5 Å,[13] even though some polymers, such as poly($n$-alkylacrylate), consist of polar functional groups on a hydrophobic backbone. In contrast, the spacing between polymer chain ($d''$) grows with increasing values of $n$ (eq 2),[13] where $n$ is the number

$$d'' = d_0 + an \tag{2}$$

of methylene units in the side chain, $d_0$ is the "effective diameter" of the backbone chain, and $a$ is the side chain length increment for each $CH_2$ group. The values of $d''$ can be used to judge the conformation of the side chain. The difference between $d''$ value (9.4 Å) for polyoctenol and $d''$ value (12 Å) for polyoctene from eq 2 is significant. It may be relative to strong intermolecular interactions resulting from hydrogen bonding.

## Experimental Section

**General Comments.** The organabornaes and Ziegler–Natta catalyst were always handled under an inert atmosphere of nitrogen or argon with careful exclusion of both oxygen and water. All glassware, syringes, and needles were oven dried at 150 °C for 2 h before use. The hot glassware was assembled while being cooled under a flow of nitrogen or evacuated in a pumping chamber before moving into the drybox.

**Materials and Equipment.** All dienes (Wiley), olefin (Aldrich), 9-BBN (Aldrich), $Al(Et)_2Cl$ (Aldrich), and $TiCl_3$·AA (Stauffer) were used as received. Analytical grades of toluene and THF were stirred with sodium naphthalide to remove traces of water and oxygen and distilled under nitrogen.

IR and $^1H$ spectra were obtained on a Perkin-Elmer 298 infrared spectrophotometer and JEOL FX90Q spectrometer, respectively. Molecule weight distributions were determined by operating a Waters GPC 150 at room temperature, elution speed 1.2 mL/min with THF as solvent. The calibration curve was obtained from 13 samples of polystyrene. GC analysis of alcohols was carried out by using a HP 5880A gas chromatograph with a 6 ft × $^1/_8$ in. 55 column, 10% Carbowax 20m on 80/100 supelcoport. Thermal properties of the polyalcohol were evaluated on a Perkin-Elmer TGS-2 thermogravimetric analyzer and a DSC-2 differential scanning calorimeter. The DSC measurements were done under a $N_2$ atmosphere at a heating rate of 20 °C/min. The TGA analysis was carried out in oxygen or Ar atmosphere (flow rate = 100 $cm^3$/min). A sample size of ~10 mg and a heating rate of 10 °C/min were used. The X-ray patterns were recorded on a Simens D-500 diffractometer. The polyoctenol employed for X-ray study was a polymer solid that was prepared by the same method described in the polyoctenol section, without any further physical treatment.

**Monomer Synthesis.** A dry 500-mL flask was equipped with a magnetic stirring bar and a connecting tube leading to a nitrogen source. The flask was thoroughly flushed with nitrogen before the injection inlet was capped with a rubber septum. A slight positive pressure of nitrogen was maintained thereafter. The flask was charged via syringe with 60 mL of octadiene. To the stirred diene solution was then added (via syringe) 200 mL of 0.5 M 9-BBN–THF solution. Sufficient time was allowed to ensure complete reaction; then the solvent and unreacted diene were recovered by reducing the pressure. *B*-7-Octenyl-9-BBN monomer (19.4 g, 84%) was distilled at 140 °C under 10-μm pressure. Spectroscopic evidences in Figures 1 and 2 confirmed the expected molecular structure of the monomer. Following the same procedure, *B*-5-hexenyl-9-BBN and *B*-4-pentenyl-9-BBN were also obtained in good yields. All monomers need to be stored in an inert atmosphere. A rapid oxidation was observed (IR spectrum) after the sample was exposed to air for a short period of time.

**The Stability of Boranes in Ziegler–Natta Catalyst.** A dry flask, equipped with a septum inlet and magnetic stirrer, was charged with 2.43 g (12 mmol) of $TiCl_3$·AA and 2.91 g (24 mmol) of $Al(Et)_2Cl$ in a drybox. After the system was flushed with nitrogen and maintained under a pressure of the gas, 5 g (24 mmol) of *B*-hexyl-9-BBN was added into the catalyst solution with the aid of a syringe. The mixture was well-stirred at room temperature overnight; no visible reaction occurred after that time. The heterogeneous catalyst complex was then removed from the mixture by filtration under an argon atmosphere, and the unreacted (>4 g) *B*-hexyl-9-BBN was recovered by distillation from the filtrate under reduced pressure (20 μm) at 130 °C.

**Polyborane.** In a typical example, 0.5 mmol of $TiCl_3$·AA, 4 mmol of $Al(Et)_2Cl$, and 64 mL of toluene were added to a 500-mL, four-necked flask under an Ar atmosphere. After sufficient mixing, 43 mmol of *B*-octenyl-9BBN monomer was added and the resulting mixture was mechanically stirred at room temperature. A viscous polymer solution was observed within 1 h. After 2 h, the high viscosity gel climbed up the stirrer. The polymerization was then stopped and precipitated by adding 200 mL of 2-propanol. The resulting precipitate was collected by filtration under a $N_2$ atmosphere. The sample was washed with 2-propanol several times and then dried in a vacuum. The IR spectrum (Figure 1b) of the resulting polymer shows the molecular structure of poly(*B*-7-octenyl-9-BBN). The overall yield in this experiment was above 90% with the weight-average molecular weight above one million. Poly(*B*-5-hexenyl-9-BBN) and poly(*B*-4-pentenyl-9-BBN) were also prepared by similar procedures.

**Polyalcohol Synthesis.** In an inert atmosphere, the polyborane, such as poly(*B*-7-octenyl-9-BBN) (5–6 g), was dissolved in 400 mL of the THF solution. A 5.3 mL (6 N) of NaOH solution was injected into the reactor, followed by dropwise addition of 10.7 mL of 33% $H_2O_2$ at 0 °C for over 15 min. The resulting mixture was then heated at 50 °C for 2 h to complete the reaction. After the solution was cooled to room temperature, the polymer was precipitated from solution by adding 200 mL of hexane. Further purification was carried out by redissolving the polymer in 1-propanol and reprecipitating polymer from petroleum ether. The resulting wet polymer adhered to glass and metal. After the polymer was dried in a vacuum oven for 2 days, a glassy like polyoctenol was obtained.

## Conclusion

Interest in the functionalization of linear hydrocarbon polymers stems from the significant enhancement of the physical, mechanical, and rheological properties of this important class of polymers. Advances in the combination of borane chemistry and Ziegler–Natta catalysis have demonstrated a new possibility to synthesize a broad range of functional polymers. Homopolymers and copolymers with a variety of other functionalities, e.g., acids, amines, etc., are being investigated. The polymerizability of borane-containing α-olefins in different catalyst systems will be reported later.

**Acknowledgment.** Numerous discussions with Dr. D. N. Schulz led me to the research of functional polymers. Discussions with Professor H. C. Brown were very helpful in understanding boron chemistry. I also wish to acknowledge Drs. R. V. Kastrup and I. Duvdevani for their contribution in NMR and DSC measurements. E. Berluche is to be thanked for his efforts in performing part of the experimental work.

**Registry No.** *B*-7-Ocetnyl-9-BBN (homopolymer), 111256-24-7; 5-hexenyl-9-BBN (homopolymer), 112741-06-7; 4-pentenyl-9-BBN (homopolymer), 112741-08-9; $TiCl_3$, 7705-07-9; $Al(Et)_2Cl$, 96-10-6.

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