Organoborane-Mediated Synthesis of Functional Polymers: A Review

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ABSTRACT

This article reviews recent advances in the synthesis of polar functional polymers via the mediation of organoborane monomers and polymers. Both direct polymerization and post-polymerization functionalization processes are described. Organoborane-assisted Ziegler–Natta, metathesis, and hydroboration (haloboration) polymerizations are presented. Moreover, the special problems and opportunities of polymer modification of olefin containing homo and copolymers by organoboranes are discussed.

INTRODUCTION

Functional polymers are macromolecules containing functional groups that have polarity or reactivity differences from backbone chains. These groups might be $-OH$, $-COOH$, $-COO^-$ on hydrocarbon backbones or hydrophobic groups on water-soluble backbones. Functional polymers often show unusual or improved properties by virtue of enhancements in phase separation, reactivity, or associations.
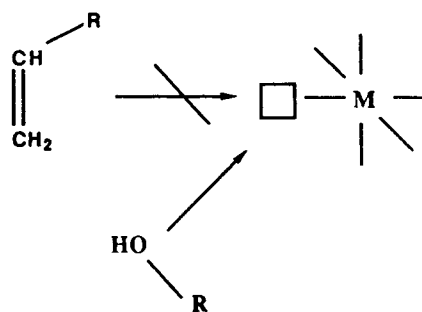
There are two basic ways to functionalize polymers; i.e., direct polymerization or post-polymerization modification. Each method has inherent synthetic difficulties. For example, the direct polymerization of polar monomers by organometallic catalysis is often plagued by catalyst poisoning by the functional group(s). Alternatively, post-polymerization modification can be hindered by solubility/gelation problems.

This article reviews recent advances in the synthesis of polar functional polymers via the mediation of organoborane monomers and polymers. Both direct polymerization and post-polymerization functionalization processes are described.

Ziegler–Natta Polymerization

Perhaps the most desirable way to prepare functional polymers is by the direct polymerization of functional monomers. However, polymers prepared by organometallic catalysts generally cannot be prepared by this method because functional groups (e.g., $-OH$, $-NH_2$, $-COOH$) preferentially coordinate with the active sites and poison the catalyst.

For example, Ziegler–Natta (Z–N) polymerization of olefins normally involves reduction of transition metal (e.g., Ti) catalysts by alkyl aluminum cocatalysts, followed by monomer complexation and insertion [1] (Equations 1–3).

$$\text{TiCl}_x \ + \ \text{Al(Et)}_3 \longrightarrow$$

$$+ \ \text{Et}_2\text{ AlCl} \quad (1)$$

I

Complexation

$$\text{I} + \quad \text{CH}_2\!\!=\!\!\text{CHR} \longrightarrow$$

$$(2)$$

II

II   **Insertion** / **Migration** $\longrightarrow$

$$(3)$$

Functional groups deactivate the catalyst and limit monomer complexation and consequent polymer formation.

Chung [2] has shown that the problem of Ziegler–Natta catalyst poisoning can be overcome by use of organoborane monomers/polymers. Organoboranes, especially cycloalkyl ones, are stable to Ziegler–Natta catalysts and have good solubility in hydrocarbon solvents, the usual solvents for Z–N processes. Moreover, as shown by the pioneering of work of H. C. Brown [3], such organoboranes are remarkably versatile synthons.

Thus, attachment of a substituted borane (e.g., 9-borobicyclononane (9BBN)) to a polymerizable olefin results in a functional monomer that can be readily polymerized by Al/Ti catalysts (Equation 4).

$$(4)$$

The conversion to polymer is quantitative as shown by ^{11}BNMR (i.e., a single resonance at 88.2 ppm). Moreover, the polyborane is easily oxidized to polyalcohol under mild conditions [2] (Equation 5).

$$(5)$$

Best results are obtained when the spacer group R is C_3 or higher. When isotactic catalysts are used, the final product is an isotactic polymer. Both homopolymers [2] and copolymers [4] are possible, depending on the presence or absence of other co-monomers. For example, a random copolymer of 1-octene and hexenyl-9-BBN [4] can be formed.

On the other hand, methyl boranes (e.g., 1-oc-tenyldimethylborane) do not polymerize under similar conditions. Ramakrishnan [5] has shown that such methyl boranes undergo a methyl group exchange with the alkylaluminum cocatalysts (Equation 6).

$$\text{Et}_2\text{AlCl} \ + \ \text{RB(Me)}_2 \longrightarrow \ \text{Et}_x\text{Me}_{2-x}\text{AlCl} \ + \ \text{RBEt}_2$$

$$(6)$$

Ring Opening Metathesis (ROMP) Polymerization

Ring opening metathesis polymerization (ROMP) is another well-known polymerization catalyzed by organometallics (Equation 7).

$$(7)$$

Although metathesis catalysts tend to be more robust than Ziegler–Natta ones, they still are readily deactivated by protic functional groups (e.g., –OH) [6]. Use of borane functional monomers/polymers allows the formation of functional polymers via the metathesis process. An example is the synthesis of poly(exo-5-hydroxynorbornene) by metathesis (Equations 8, 9).

(8)

(9)
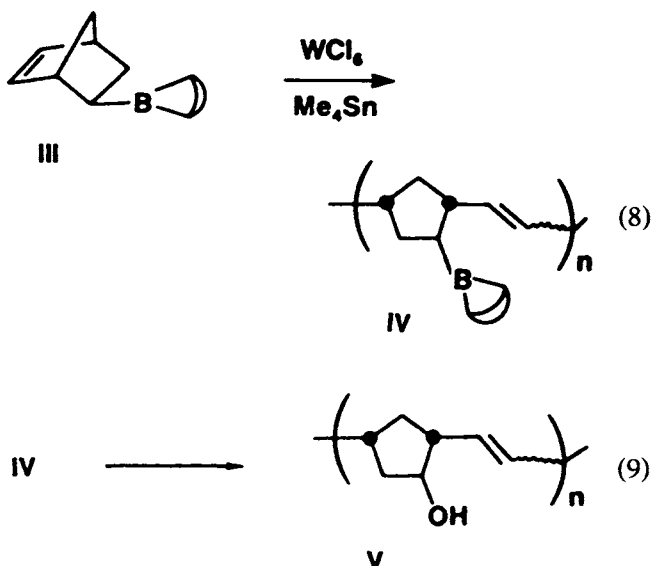
The monomer, exo-B-5-norborn-2-enyl-9-BBN (**III**), is synthesized by selective hydroboration of 2,5-norbornadiene with 9-BBN, using a 4-fold excess of the diene, to minimize the formation of the bis adduct [7].

Three catalysts have been used for the polymerization of norbornenyl-9-BBN (Table 1). The resulting polynorbornenyl-9-BBNs have almost the same molecular weight as nonfunctional polynorbornenes prepared under the same polymerization conditions. WCl_6/Me_4Sn gives a polymer with almost equal amounts of cis and trans double bonds. The Lewis-acid free catalyst of W(CHt-Bu)-

(NAr)(OCMe[CF₃]₂)₂ yields a high cis polymer. This catalyst has been shown to produce high cis-polynorbornene that is isomerized to high trans-polymer upon extended polymerization times. However, in the case of norbornenyl-9-BBN, no isomerization is observed even after polymerization times of up to 60 h. This difference in behavior may be caused by the presence of the large 9-BBN substituent on the polymer, which shields the double bonds on the backbone. Because the tungsten carbene is sterically protected, it is difficult to form the metalocyclobutane intermediate, which is required for isomerization. On the other hand, when the less reactive W(CHt-Bu)(NAr)(Ot-Bu)₂ is used, a high trans (76%) polymer is formed. Oxidation of these borane polymers yields exo-poly(5-hydroxy-norbornene)s with different cis-trans compositions [7].

ROMP chemistry has also been extended to the preparation of linear functional polymers, particularly alternating vinyl alcohol type copolymers; e.g., poly(vinylalcohol-co-ethylene) and poly(vinyl alcohol-co-ethylene-co-1,4-butadiene) [8]. This chemistry involves ring opening metathesis polymerization (ROMP) of cyclooctenylborane monomer **VI**. The linear polymer **VII** obtained in this process has borane groups homogeneously distributed along the polymer chains as shown in Scheme 1.

The monomer (**VI**) is polymerized using a Lewis-acid free metathesis catalyst, W(CHt-Bu)(NAr)-(OCMe[OCF₃]₂) [13]. The polymerization occurs very rapidly, and the polymer (**VII**) formed is oxidized, using alkaline H₂O₂, to give hydroxy polymers (**VIII**) and (**IX**). Polymer **IX** has a novel regular structure composed of vinyl alcohol, ethylene, and 1,4-butadiene units. The unique feature of this product is that the arrangement of the comonomer units (i.e., vinyl alcohol, ethylene, and 1,4-butadiene) along the backbone is completely fixed by the starting cyclic monomer structure (**VI**). Only subtle variations in the comonomer arrangement (e.g., head-to-head, head-to-tail, etc.) still remain to be defined. Polymer (**IX**) is quite soluble in many organic solvents, such as THF/chloroform. The ¹H

TABLE 1 A Summary of Poly(exo-5-hydroxynorbornene) Prepared by Three Tungsten Catalysts

Sample/Catalyst	Reaction Time (h)	Yield (%)	Cis Content (%)	Mn	Mw/Mn
PNBEOH[a]/ W(CHt-Bu)(NAr)(OCMe[CF₃]₂)₂	2	95	93	270,204 34,833	bimodal
PNBEOH[a]/ WCl₆/Me₄Sn	2	84	48	58,198	2.3
PNBEOH[a]/ W(CHt-Bu)(NAr)(Ot-Bu)₂	2	95	26	63,211	1.6

[a] Poly(5-hydroxynorbornene).

SCHEME 1

SCHEME 2
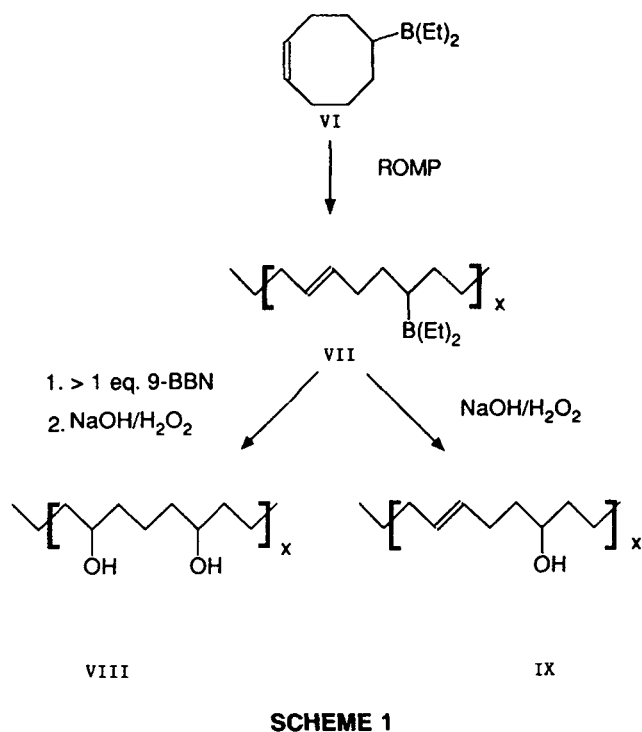
NMR spectrum of polymer (**IX**) shows the expected relative integral intensities for the vinylic (5.5 ppm) and allylic (~2.05 ppm) protons.

The borane polymer (**VII**) can be further modified by hydroboration with 9-BBN, prior to oxidation. Use of a stoichiometric amount of a hydroborating reagent results in poly(vinyl alcohol-*co*-ethylene) after oxidation. This polymer has an exact 50/50 copolymer composition with alternating microstructure (**VIII**). The ^{1}H NMR spectrum of polymer (**VIII**) shows the complete absence of vinylic protons at 5.5 ppm. The alternating copolymer of poly(vinyl alcohol-*co*-ethylene) is soluble only in mixed solvents, such as THF/methanol and chloroform/methanol. The molecular weight of this polymer (**VIII**), after acetylation, has been determined (by GPC in THF) to be 340,000 with a polydispersity of 2.8.

Telechelic Polymers via Metathesis

It is well known in metathesis chemistry that the cometathesis of an olefinic polymer and small molecule olefin leads to lower molecular weight products [9] (Equation 10).
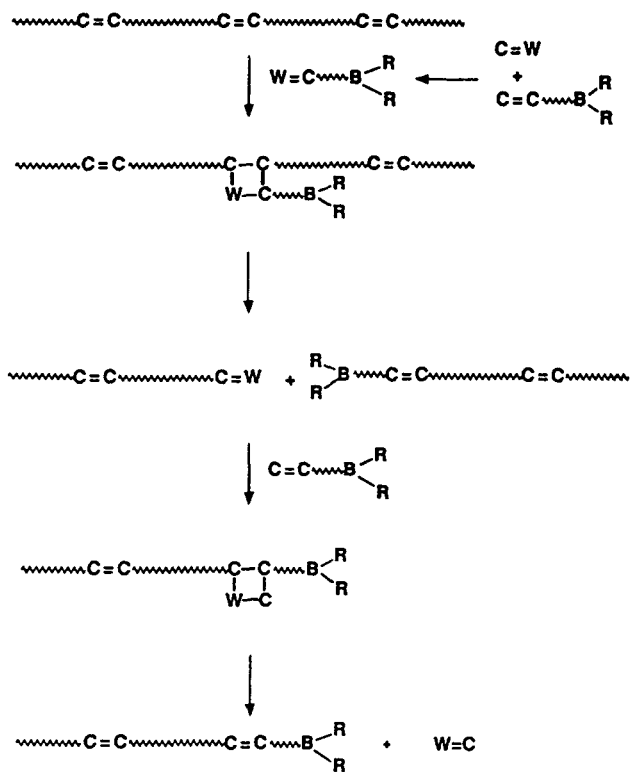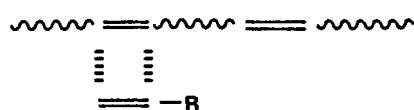
Chung and co-workers [9] have advantageously combined this concept with organoborane containing olefins to yield functionally terminal (telechelic) polymers (Scheme 2). Specifically 1-hexenyl-6-(9 BBN) is added to a solution of 1,4-polybutadiene. The metathesis reaction is initiated by the addition of $WCl_6/Sn(Me)_4$. The viscosity of the polymer solution decreases significantly during the reaction. After termination and oxidation the product is an α,ω-dihydroxy-1,4-polybutadiene.

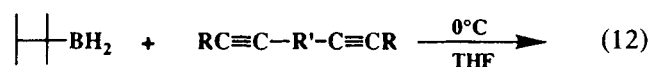### Hydroboration and Haloboration Polymerization

Recently, Saegusa [10, 11] extended Brown's [3, 12, 13] work on the polyaddition of dienes with monalkylboranes. For example, thexylborane is reacted with 1,7-octadiene to produce linear organoborane polymers (Equation 11).

$$ (10) $$

$$\text{H}_2\text{B}\!-\!\text{BH}_2 \;+\; \overset{}{\diagup}\text{R}\overset{}{\diagdown} \quad\xrightarrow[\text{THF}]{0^\circ\text{C}}$$

 (11)
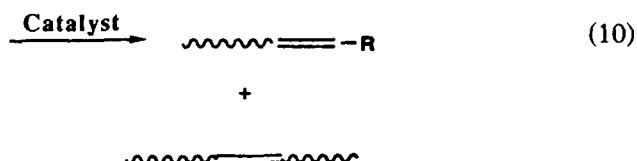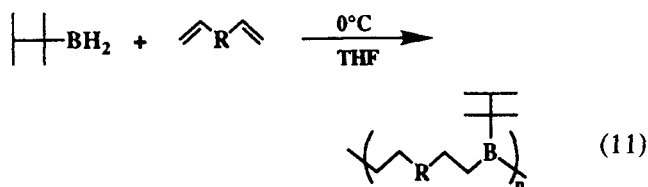
These organoborane polymers are stable to protic solvents such as water and alcohol but must be kept under nitrogen [11].

In turn, diynes (e.g., 2,9-dodecadiyne) can be substituted for dienes to form essentially gel-free organoboron polymers of unknown structure [14] (Equation 12).

$$\text{H}_2\text{B}\!-\!\text{BH}_2 \;+\; \text{RC}{\equiv}\text{C}\!-\!\text{R}'\!-\!\text{C}{\equiv}\text{CR} \quad\xrightarrow[\text{THF}]{0^\circ\text{C}} \quad (12)$$

Organoboron

Polymers

However, use of terminal diynes (e.g., 1,7 octadeyne) leads to branched and cross-linked materials [14].

The linear organoboron polymers can be regarded as homologues of trialkylborane and can be expected to be convertible to other functionalities, as shown by Brown [3] for organic compounds. For example, the reaction of the linear organoboron polymers with carbon monoxide at 120°C, followed by oxidation, results in the exclusive formation of polyalcohols via migration of C–B bonds [15, 17] (Equation 13).
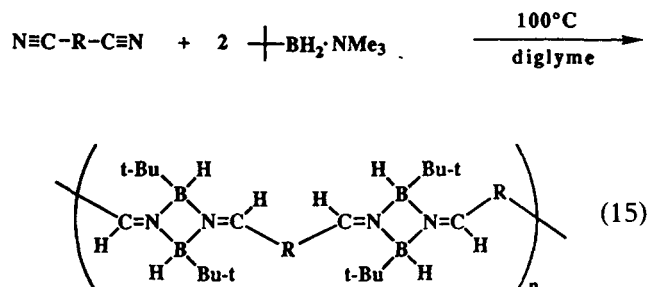
 (13)
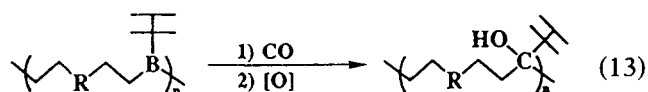
However, under milder conditions (i.e., 50°C) the polymer obtained consists of a copolymer of poly(alcohol) and poly(ketone) [15–17].
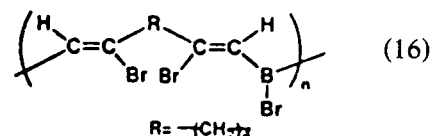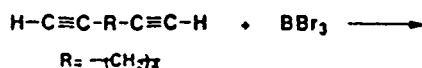
On the other hand, poly(ketone) homopolymers can be prepared by reaction of the organoborane adduct of thexylborane and 1,7-octadiene with potassium cyanide in the presence of trifluoracetic anhydride (TFAA) [15, 18] (Equation 14).

 (14)
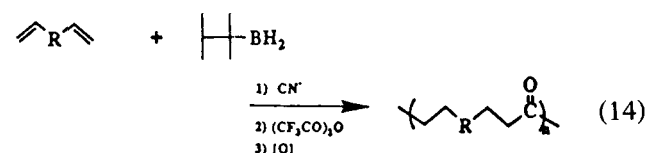
In addition, hydroboration polymerization of dicyano compounds (i.e., *t*-butylborane with isophthalonitrile) yields an air-stable boron containing polymer having B–N four-membered rings via dimerization of iminoborane species [19] (Equation 15).

$$\text{N}{\equiv}\text{C}\!-\!\text{R}\!-\!\text{C}{\equiv}\text{N} \;+\; 2\;\text{H}_2\text{B}\!-\!\text{BH}_2\!\cdot\!\text{NMe}_3 \quad\xrightarrow[\text{diglyme}]{100^\circ\text{C}}$$

 (15)

Haloboration involves polyaddition of diacetylene and boron tribromide to form linear poly(organoboron halide) [20] (Equation 16).

$$\text{H}\!-\!\text{C}{\equiv}\text{C}\!-\!\text{R}\!-\!\text{C}{\equiv}\text{C}\!-\!\text{H} \;+\; \text{BBr}_3 \longrightarrow$$

$$\text{R}= -(\text{CH}_2)_n-$$

 (16)

$$\text{R}= -(\text{CH}_2)_n-$$

This polymer still has B–Br bonds in its structure. It is not only a novel, reactive polymer but also may be regarded as a polymeric Lewis acid.
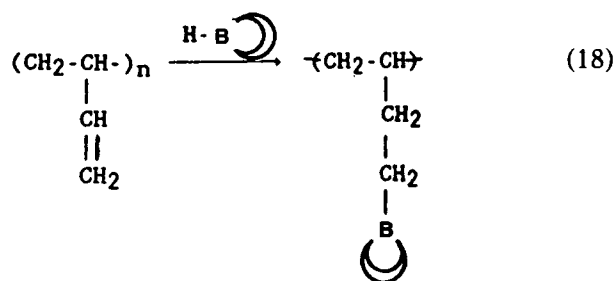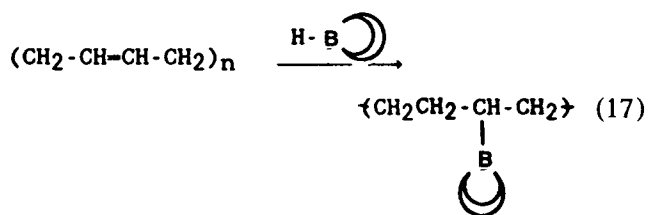
Post-Polymerization Modification

In principle, any reaction of classical organic chemistry can be applied to modifying/functionalizing polymer chains. However, the kinetics and mechanisms of reactions on polymers can be quite different from those of small molecules.

For example, the reactivity of functional groups on polymers depends on (a) the composition and length (molecular weight) of the chain, (b) the solubility of both reactants and polymers, (c) the morphology and history of the macromolecule, and (d) the medium (e.g., solution, melt) and reactor (e.g., stirred tank, extruder) type. In addition, chemical reactions on polymers have the added concerns of backbone-specific side reactions; i.e., chain scission (degradation) or cross-linking (gelation) [21–23]. The most ideal chemical modifications on polymers are the so-called polymer analogous reactions, where the polymer is converted to a derivative macromolecule of equivalent backbone chain length with a minimum of gel content [24].

Some of the most highly studied polymer modifications are reactions on polydienes (e.g., polybutadiene, polyisoprene) because of the rich chemistry of the olefinic double bond. For example, such olefinic polymers have been isomerized, hydrogenated, halogenated, epoxidized, metalated, and sulfonated, as well as being sites for Diels Alder or 'ene processes. The chemical modification of polydienes has been the subject of several recent reviews [25, 26].

Of course, hydroboration is a very selective reaction and the corresponding organoborane intermediates are among the most versatile intermediates in organic chemistry [3]. Yet, until recently, hydroboration of polydienes has received comparatively little attention, probably because this polymer modification has been plagued by the side reactions of chain degradation and/or gelation [27–29].

Chung and co-workers [30] have studied the hydroboration of 1,4-and 1,2-polybutadienes and have learned how to conduct this reaction in the absence of chain scission or cross-linking (Equations 17, 18).
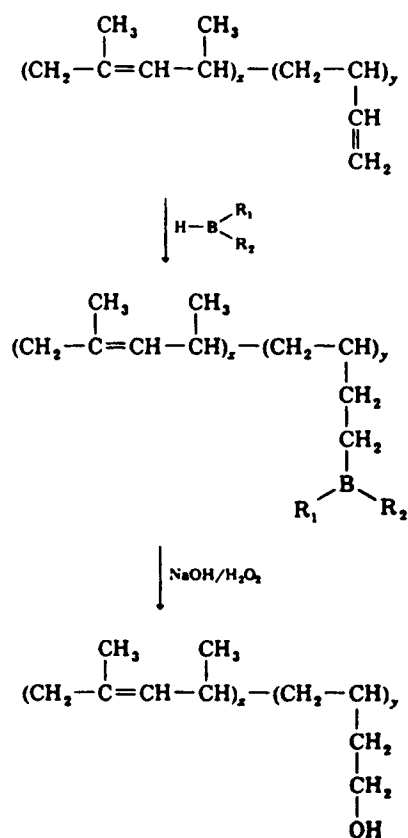
$$(CH_2\text{-}CH\text{=}CH\text{-}CH_2)_n \xrightarrow{\text{H-B}} $$

$$\{CH_2CH_2\text{-}\underset{|}{\underset{B}{C}}H\text{-}CH_2\} \quad (17)$$

$$(CH_2\text{-}\underset{|}{\underset{CH}{C}}H\text{-})_n \xrightarrow{\text{H-B}} \{CH_2\text{-}\underset{|}{\underset{CH_2}{C}}H\} \quad (18)$$

Specifically, they found that the key to producing a gel-free product is the use of a monofunctional dialkyl borane, such as 9-borobicyclo-[3.3.1]-nonane (9-BBN), and the presence of an oxygen-free reaction environment. Both conditions minimize the presence of adventitious free radicals that can cause cross-linking and/or a broadening of the polymer molecular weight distribution (MWD). The resulting hydroborated 1,2-polybutadiene has a single trialkylborane resonance in the ^{11}B NMR spectrum at 87.5 ppm (vs. BF$_3$·OEt$_2$), indicating the absence of side reactions.

The oxidation of the polyborane to the polyalcohol also requires special care because the products of the oxidation are not only the polyalcohol but also low molecular weight impurities; e.g., cyclic alcohol and boric acid/salt (Equation 19).

$$\{\text{-B} + NaOH + 3H_2O_2 \rightarrow \{\text{-OH} + \text{(cyclooctane diol)} + \quad (19)$$

$$NaOB(OH)_3$$
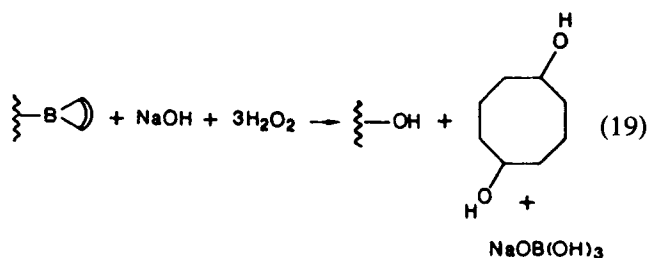
Standard polymer isolation techniques, such as precipitation from a nonsolvent, are acceptable for removing the cyclic alcohol, but not the salt of boric acid. Unfortunately, the residual sodium borate can act as a cross-linking agent for the hydroxylated polymer. Chung and co-workers [30] have solved this problem by azeotropic removal of boric acid as a complex with methanol. The absence of chain scission and cross-linking has been proven by GPC. The MWD of the polymer before and after hydroboration/oxidation is essentially the same; i.e., less than 1.1. Ramakrishnan [31] has recently extended these methods to the hydroboration of polyalkenylenes, such as polypentenamer.

As shown in Brown's work on small molecules [3], external double bonds are much more reactive

$$(CH_2\text{-}\underset{|}{\underset{CH_3}{C}}\text{=}CH\text{-}\underset{|}{\underset{CH_3}{C}}H)_x\text{-}(CH_2\text{-}\underset{|}{\underset{CH}{\underset{\parallel}{CH_2}}}CH)_y$$

$$\downarrow \text{H-B}\overset{R_1}{\underset{R_2}{}}$$

$$(CH_2\text{-}\underset{|}{\underset{CH_3}{C}}\text{=}CH\text{-}\underset{|}{\underset{CH_3}{C}}H)_x\text{-}(CH_2\text{-}\underset{|}{\underset{CH_2}{\underset{|}{\underset{CH_2}{\underset{|}{\underset{B}{R_1\,R_2}}}}}}CH)_y$$

$$\downarrow NaOH/H_2O_2$$

$$(CH_2\text{-}\underset{|}{\underset{CH_3}{C}}\text{=}CH\text{-}\underset{|}{\underset{CH_3}{C}}H)_x\text{-}(CH_2\text{-}\underset{|}{\underset{CH_2}{\underset{|}{\underset{CH_2}{\underset{|}{OH}}}}}CH)_y$$

SCHEME 3

than internal ones toward hydroboration. Thus, 1,2-polybutadiene units can be selectively hydroborated in the presence of 1,4-polybutadiene, 2,4-polyisoprene, or poly(2-methyl-1,3 pentadiene) segments even if such structures are on the same chain [32].

Scheme 3 shows the selective hydroboration/oxidation of a block copolymer of poly(2-methyl-1,3-butadiene) and 1,2-polybutadiene.

Other workers [33] have used the hydroboration of 1,2-polybutadiene as a stepping-stone toward the preparation of monodisperse liquid crystalline side-chain polymers. Specifically, 1,2-polybutadiene is hydroborated with 9-borabicyclo[3.3.1]nonane, followed by oxidation to the corresponding alcohol (Equation 20).

$$\text{(20)}$$
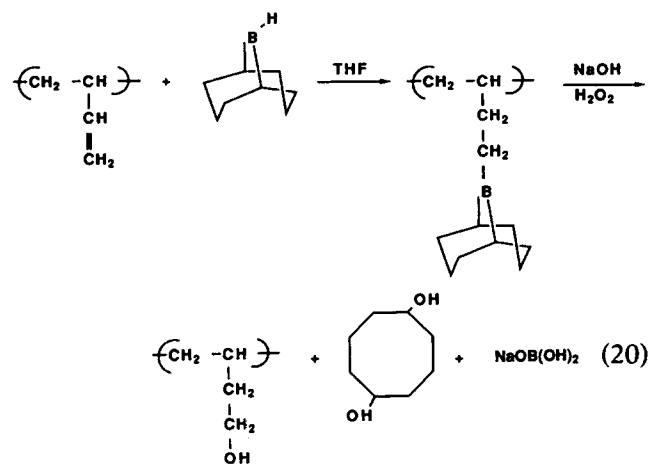
The mesogenic units are then connected to the polyalcohol via ester or carbonate linkages (Equation 21).

$$\text{(21)}$$
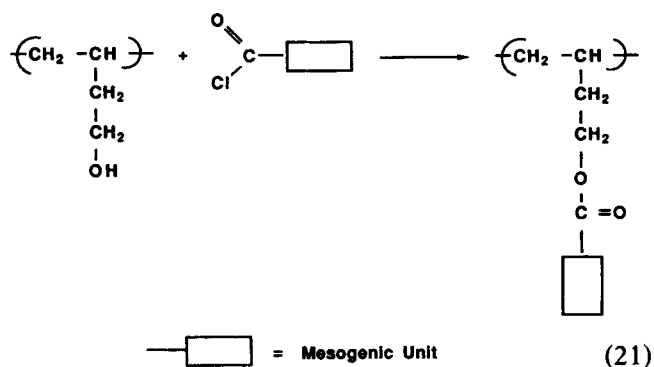
SUMMARY

This article reviews the advantageous use of organoborane monomers and polymers for the synthesis

of functional polymers. Both direct polymerization and post-polymerization functionalization methods are described. Citations within the past several years are featured.

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