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Synthesis of Novel Boron-Containing Polymers and Related Reactions

Ikuyoshi TOMITA

1993

PREFACE

The studies presented in this thesis have been carried out under the directions of Prof. Takeo Saegusa and Dr. Yoshiki Chujo at Kyoto University during 1988-1991. The studies are concerned with the synthesis of novel boron-containing polymers and related reactions.

The author wishes to express his sincerest gratitude to Professor Takeo Saegusa for his valuable guidance, instructive suggestions, and heartfelt encouragement. The author is also extremely grateful to Dr. Yoshiki Chujo for his constant advice, very useful discussions, sharp insights, and very kind encouragement. The author would like to thank Messrs. Yuichi Hashiguchi, Nobuhide Murata, Tsuyoshi Asano, Yuji Kozawa, Masao Morimoto, Miss Heike Mauermann, and Dr. Tilman Krauch for their active collaborations. He also thanks to Drs. Masato Suzuki, Kazuki Sada, Kensuke Naka, Keigo Aoi, Eiji Ihara, and Mr. Akio Naka, and all the members in Professor Saegusa's laboratory for their useful suggestions and enjoyable times.

The author appreciates greatly to Prof. Takeshi Endo at Tokyo Institute of Technology for kindly directing the author and arranging the opportunity to publish this thesis. The author expresses a sense of gratitude to him also for his useful and kind-hearted instructions for the new works of the author at Tokyo Institute of Technology.

The deepest gratitude is made to Prof. Toshinobu Higashimura at Kyoto University for offering the chance to the author to extend the work in this thesis for one more year under his heartfelt directions.

Finally, the author wishes to express his deep appreciation to his parents, Mr. Toshio Tomita and Mrs. Eiko Tomita, and his fiancee, Miss Naoko Kitaoka, for their constant assistance and heartfelt encouragement.

Ikuyoshi Tomita

September, 1993

CONTENTS

Chapter 1

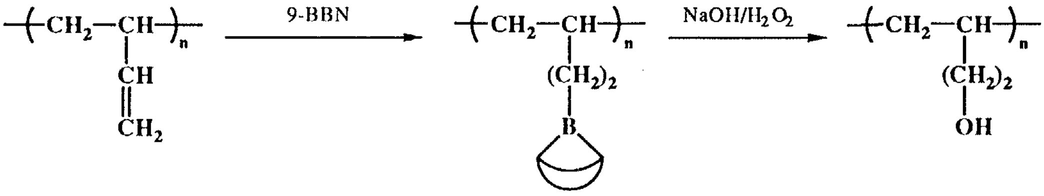
General Introduction

GENERAL INTRODUCTION

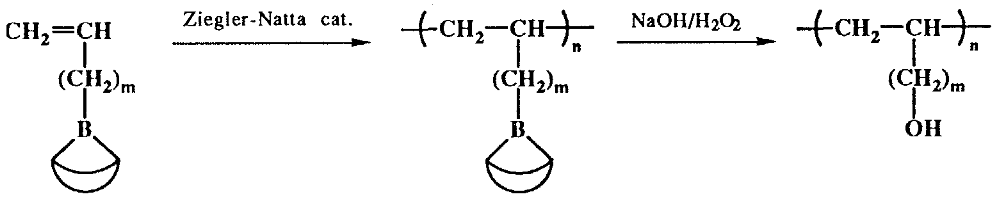
For these several decades, the organoboron chemistry has been developed with the discovery of hydroboration$^{1)}$. Especially, a wide variety of reactions starting from (or *via*) organoboron compounds have been developed in the field of organic synthesis$^{2)}$. As a result, organoboron compounds are taken to play an important role as useful intermediates in organic synthesis. In spite of the importance of these compounds as intermediates in organic synthesis, a few studies have been carried out to utilize these compounds as functional materials. For instance, the aromaticity as well as *anti*-aromaticity of conjugated organoboron heterocycles through vacant *p*-orbitals of boron atoms have been carefully studied$^{3)}$.

In the field of polymer synthesis, however, only a few reports have dealt with the synthesis of organoboron polymers$^{4)}$, presumably because these materials were believed to be too unstable for the practical use. The use of organoboron compounds in the polymer synthesis has been also limited for initiators in vinyl polymerization$^{5)}$, polymer reactions of 1,2-poly(butadiene) followed by the oxidative treatment to produce poly(alcohol)s (Scheme I)$^{6)}$, the maskings of double bond in vinyl polymerization to produce poly(alcohol)s (Scheme II)$^{7)}$, and an inert functional group in cyclic olefins that undergo ring-opening olefin-metathesis polymerization followed by oxidation to give poly(alcohol)s (Scheme III)$^{8)}$. However, organoboron polymers bearing carbon-boron bonds in the main chain have been limited (*vide infra*) and very few reports are known about characters as well as reactivities of this type of polymers.

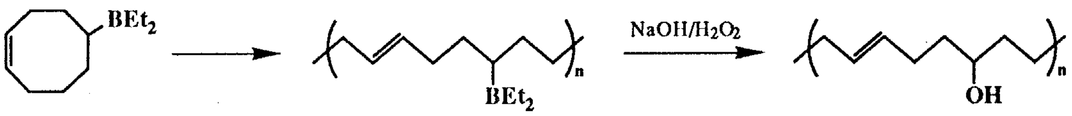
Scheme I



Scheme II

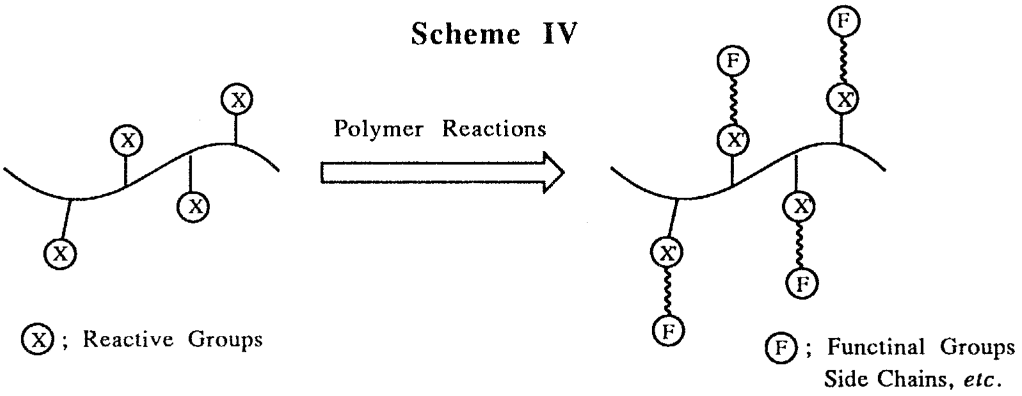


Scheme III



In spite of a wide development in the field of reactive polymers, only the polymers having reactive functional groups such as derivatives of carboxylic acids, alcohols, amines, halides, and unsaturated bonds are generally regarded as reactive polymers (Scheme IV)9). Based on the reactivity of these functional groups

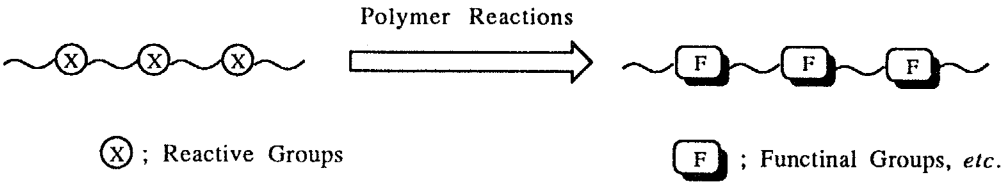
Scheme IV



in the polymer chain, side chains or other functional groups could be introduced into the polymer chains. These polymers, however, always have the reactive points in the side chain of the polymer which could not, of course, reconstruct the polymer backbone. If organoboron polymers having boron atom in the main chain were produced, a novel type of reactions that can convert to polymers consisting of different backbone structures could be possible (Scheme V).

Accordingly, it is indeed an attractive target to make polymers having boron atoms in their main chains, not only because the character of such polymers has been left unknown, but because these polymers can be regarded as a novel type of reactive polymers that can produce various functional polymers. Additionally, if it is possible to build up polymers stable under air, these polymers may potentially serve as novel materials and/or a good precursor for inorganic materials by the pyrolytic treatment.

Scheme V



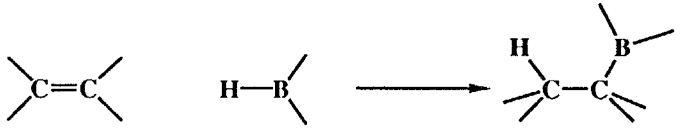
On the basis of these backgrounds, this thesis deals with syntheses of organoboron polymers by developing new synthetic methodologies, novel reactions of the obtained organoboron polymers that produce polymers having different backbone, syntheses of novel boron-containing polymers bearing boron-nitrogen four-membered structures in the main chain, other methods providing boron-containing materials, and an attempt to utilize organoboron compounds for polymer synthesis.

Survey of This Thesis

As mentioned above, this thesis describes syntheses and reactions of organoboron polymers, syntheses of novel boron-containing polymers, and polymerization reactions related to organoboron compounds. By the classification of type of reactions and type of polymers, this thesis contains five chapters (Chapters 2-6) as follows.

Chapter 2 Hydroboration Polymerization. As mentioned above, hydroboration reaction (addition of B-H to C=C, Scheme VI) is a well-known tool for the preparation of various alkylborane compounds in organic synthesis, which takes place under mild conditions almost quantitatively$^{1)}$. However, the direct use of this reaction in polymer synthesis has been very limited so far. Among numerous studies reported by Brown and his group, the formation of polymeric materials has been only described in their papers on the reaction of thexylborane with 1,3-butadiene[10)] or of monochloroborane with 1,7-octadiene[11)].

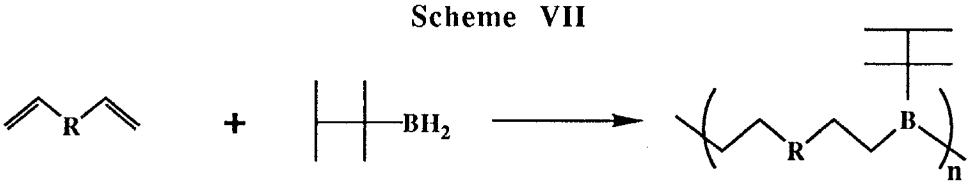
Scheme VI



These polymers were formed as intermediates to obtain boron heterocycles by the so-called thermal depolymerization. Previously, Urry *et al.* reported that the organoboron polymer was formed by the pyrolysis of 2,5-dimethyl-2,5-diborahexane[12)]. Mikhailov *et al.* also reported the formation of organoboron polymer by thermal isomerization of triallylborane and triisobutylborane[13)]. However, no detail was reported about the yield, molecular weights, and characterization (structure) of the resulting polymers. Thus, this chapter is concerned with the synthesis of novel organoboron polymers by means of hydroboration technique (i.e., "Hydroboration Polymerization").

In 2-1, hydroboration polymerization between dienes and bifunctional thexylborane to produce novel organoboron polymers is described (Scheme VII). The molecular weight of the polymer obtained increased as the feed ratio approached to unity. This effect is taken as a normal behavior of polyaddition reaction.

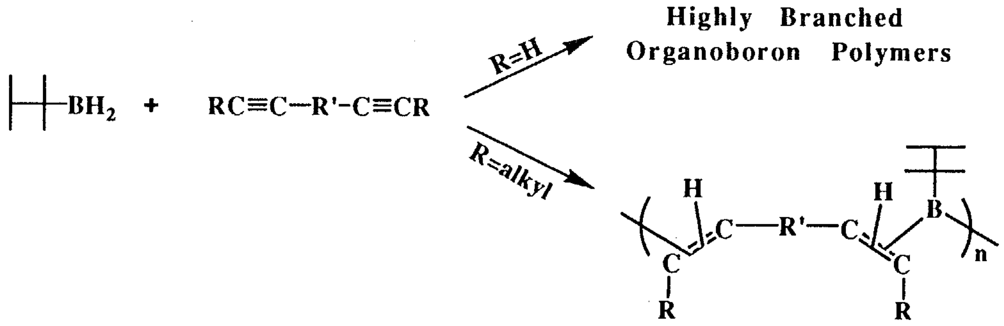
Scheme VII



The resulting organoboron polymers were isolated as a colorless gum and were soluble in common organic solvents. The structure of the polymer was supported by spectroscopic methods. These organoboron polymers were stable enough against protic solvents such as water and alcohol under nitrogen. Under air, these polymers were gradually decomposed as usual for organoboron compounds. However, these polymers were a little more stable toward air in comparison with conventional trialkylboranes.

In 2-2, hydroboration polymerizations of thexylborane with terminal diynes as well as internal diynes are described. Generally, the reactivity of a terminal acetylene toward hydroboration is quite different from that of an internal acetylene. While the terminal acetylenes preferentially give dihydroboration products *via* a further hydroboration of the initially formed vinylborane species, the internal acetylenes give monohydroboration products regardless of the bulkiness of borane used. Thus, terminal diyne and internal diyne are expected to show the different polymerization behavior due to the probability of the second (further) hydroboration reaction. In fact, hydroboration polymerization of terminal diynes gave highly branched polymers as a result of dihydroboration (i.e., attacks of B-H towards vinylboranes) and a gelation took place in the presence of excess borane monomer. The obtained gel was interestingly cleaved by the protic solvents in the absence of air. On the other hand, internal diynes gave linear polymers bearing divinylborane units in the main chain by the selective monohydroboration (Scheme VIII). The organoboron polymers obtained from diynes also showed degradations under air to produce oligomers containing ketone moieties.

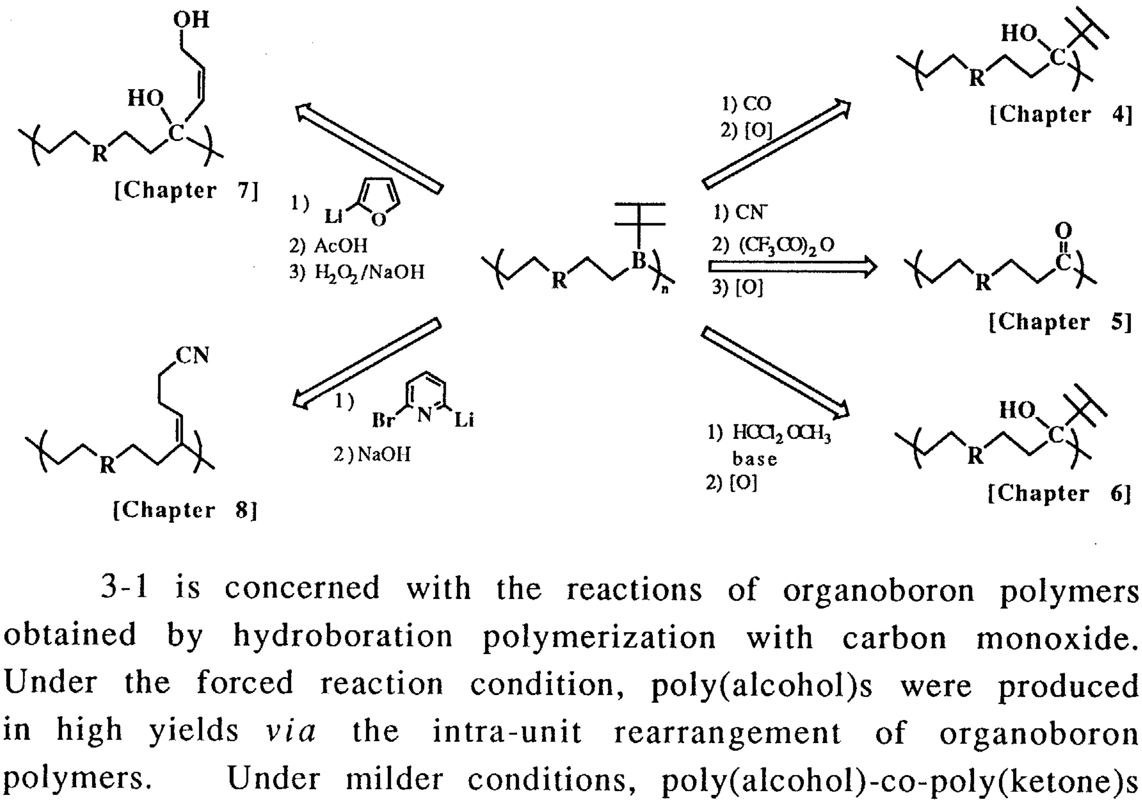
Scheme VIII



In 2-3, copolymerization of a mixture of dienes as well as that of a mixture of diene and terminal diyne are described. From the diene mixture, copolymers were obtained effectively whose molecular weight distributions indicated clear difference from that of a mixture of two homopolymers. On the other hand, when the polymerization between thexylborane and diene was carried out in the presence of a trace amount of terminal diyne, the molecular weights of organoboron polymers were found to be increased with an increase of the ratio of diyne/diene as a result of branched structure caused by the dyne monomer.

Chapter 3 Reactions of Organoboron Polymers Prepared by Hydroboration Polymerization. The organoboron polymers prepared by hydroboration polymerization have a novel structure consisting of C-B bonds in the main chain. These organoboron polymers can be regarded as a polymer homologue of trialkylborane, which is known to be a very versatile compound in organic synthesis2). In other words, the obtained polymers by hydroboration polymerization can be expected as a novel type of reactive polymers. Thus, reactions of organoboron polymers prepared from diene and thexylborane (in Chapter 2, 2-1) are described in this chapter. These results clearly demonstrate the novel reactivity of organoboron polymers (Scheme IX).

Scheme IX



3-1 is concerned with the reactions of organoboron polymers obtained by hydroboration polymerization with carbon monoxide. Under the forced reaction condition, poly(alcohol)s were produced in high yields *via* the intra-unit rearrangement of organoboron polymers. Under milder conditions, poly(alcohol)-co-poly(ketone)s were obtained as a result of insufficient migration of a thexyl group on boron atom.

In 3-2, the reaction of organoboron polymer with potassium cyanide followed by the oxidative treatment to produce a poly(ketone) is described. In this reaction system, only two alkyl groups (i.e., the main chain of organoboron polymer) except a thexyl group migrate to the carbon atom of cyanide to give poly(ketone) selectively.

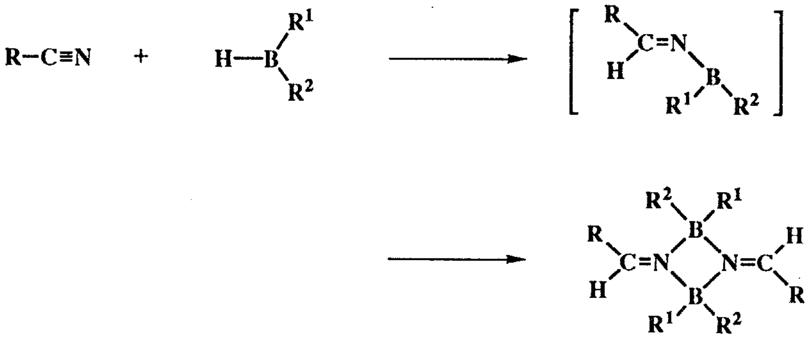
In 3-3, poly(alcohol)s were prepared in high yields by the reaction of organoboron polymers with α,α-dichloromethyl methyl ether (DCME) in place of carbon monoxide, followed by the oxidative treatment. The structures of the resulting poly(alcohol)s were same as those prepared by the reaction with carbon monoxide described above. Because the reaction with carbon monoxide requires relatively severe conditions, the reaction with DCME provides more facile way for the conversion of organoboron polymers into poly(alcohol)s under mild conditions.

Synthesis of poly(alcohol)s having primary and tertiary hydroxyl groups by the reaction of organoboron polymers with α-furyllithium is described in 3-4. This reaction includes an intramolecular (intra-unit) rearrangement of polymer chains of organoboron polymer and a ring-opening of furan rings.

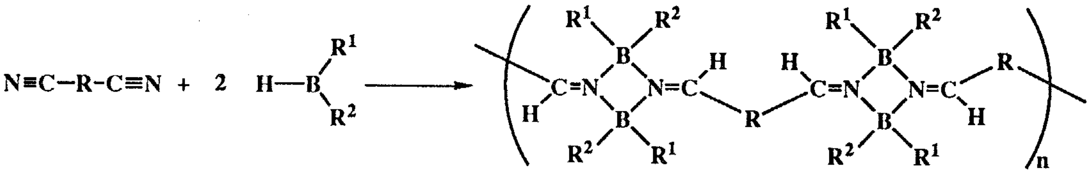
In 3-5, polymers having nitrile groups were obtained by the reaction of organoboron polymers with 2-bromo-6-lithiopyridine also *via* a similar rearrengement reaction accompanying the ring-opening of pyridine moieties. The obtained polymers had almost the same molecular weights as those of starting organoboron polymers.

Chapter 4 Synthesis of Novel Boron-Containing Polymers by Hydroboration Polymerization of Dicyano Compounds. The organoboron polymers prepared by hydroboration polymerization of dienes or diynes are relatively unstable toward air. On the other hand, the preparation of stable boron-containing polymers has been an attractive target as polymeric materials, for which a few examples such as borazine, phosphinoborane, and decarborane polymers have been reported[14]. It is known that hydroboration reaction of cyano groups gives iminoborane species which dimerize to form boron-nitrogen four-membered rings (i.e., derivatives of cyclodiborazane) in the case of appropriate borane used (Scheme X)[15]. When this reaction is applied to the bifunctional monomers, formation of air-stable polymeric materials consisting of cyclodiborazane units can be expected (Scheme XI).

Scheme X



Scheme XI



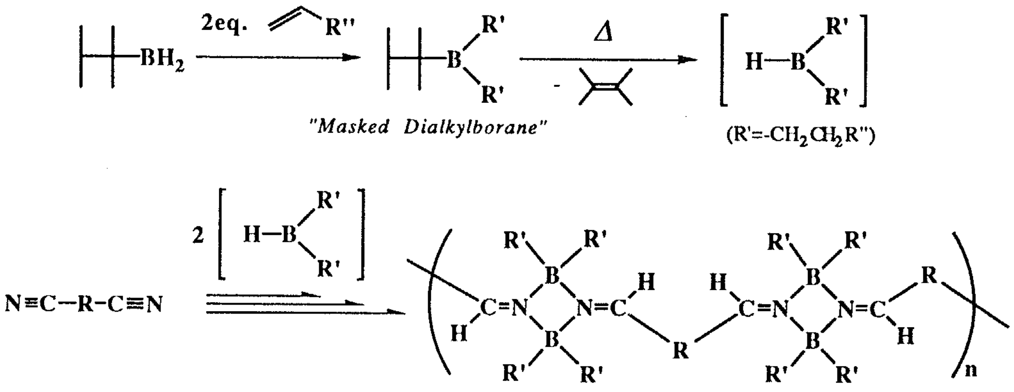
In 4-1, t-BuBH$_2$•NMe$_3$ was used as a monoalkylborane part, and the polyadditions with several kinds of dicyano monomers were examined. From the stoichiometric study using isophthalonitrile as a dicyano monomer, a small excess amount of borane was found to increase the molecular weight of the obtained polymer in this polymerization. The structure of the resulting polymer was confirmed by its spectroscopic analyses. As a dicyano compound, the monomers having aromatic cyano groups rather than aliphatic ones gave polymers with higher molecular weights in higher yields.

In 4-2, steric effects of the alkyl substituents attached to the boron atom in monoalkylborane monomers on the hydroboration polymerization were examined. When less sterically hindered monoalkylboranes such as n-BuBH$_2$•NMe$_3$ and i-PrBH$_2$•NMe$_3$ were used as a monomer, less soluble materials were obtained due to the crosslinking reaction (i.e., the formation of dibora-amines). From the reaction using thexylborane, however, α,ω-dicyanoalkanes rather than aromatic ones gave soluble oligomers. These results clarified the steric demands on the boron atom in hydroboration polymerization of dicyano monomers.

In 4-3, dialkylboranes were used as a monomer, instead of monoalkylboranes. The bulk polymerization of $(n\text{-Bu}_2BH)_2$ especially with α,ω-dicyanoalkanes gave the corresponding polymers in high yields as colorless gums within the several hours' reaction. The obtained polymers were stable under air and the molecular weights of the resulting polymers were higher than those obtained from monoalkylboranes.

In a practical point of view, preparation and isolation of dialkylboranes are difficult due to their instability. Therefore, in 4-4, thexyldialkylboranes prepared from thexylborane and the corresponding terminal olefins were used as masked dialkylboranes. In this system, dialkylboranes were generated *in situ* by the *retro*-hydroboration of thexyl group (Scheme XII). The structures of the polymers obtained in the present method were identical with those prepared from isolated dialkylborane with dicyano monomers. By using this method, dialkylboranes with longer alkyl chains could be also utilized as monomer components.

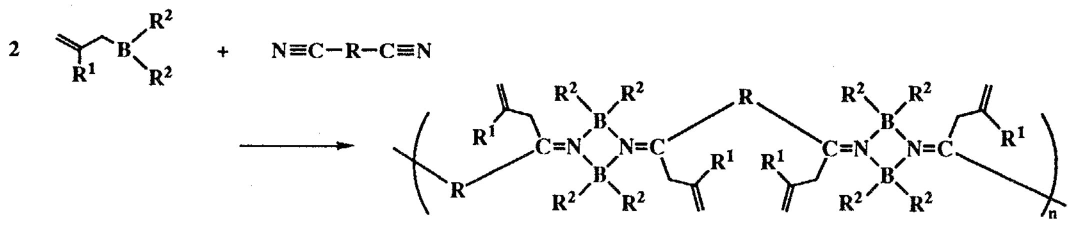
Scheme XII



All the polymers prepared by hydroboration polymerization of dicyano compounds were stable under air and gave some residue after the pyrolysis that may open a useful way to obtain boron-containing inorganic materials.

Chapter 5 Allylboration Polymerization of Dicyano Compounds and an Alternative Polymerization Reaction. Cyclodiborazanes are known to be also prepared by the reactions of nitriles with triallylborane16) or allyldialkylboranes17). Thus, the synthesis of boron-containing polymers with the similar structure consisting of B-N four-membered rings was examined by allylboration technique between allylboranes and dicyano compounds (Scheme XIII). The stability of boron-containing polymers was found to depend on the structure of the borane monomers. Similarly to the polymers prepared by the hydroboration polymerization of dicyano monomers, these polymers gave some residue after pyrolysis. For the alternative method to obtain boron-containing polymers, condensation reactions of bis(silylimine)s with substituted boranes such as chlorodialkylborane and methyl dialkylborinates are also described.

Scheme XIII



R^1= -H, or -Me
R^2= allyl, methallyl, or alkyl

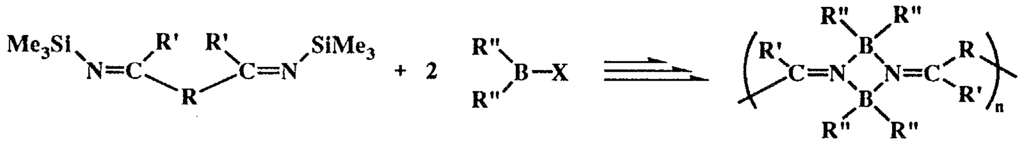
In 5-1, polymerization with triallylborane is described. When polymerization between triallylborane and isophthalonitrile was carried out in bulk at 0°C, the reaction mixture became homogeneous liquid within several minutes, became viscous and offered glassy polymer after the reaction for 1 day. The structure of the polymer was confirmed by its spectroscopic analyses. The air and thermal stabilities of the obtained polymers were examined. Most part of the boron-containing polymers became insoluble by the storage for several days.

In 5-2, boron-containing polymers were prepared from trimethallylborane. When polymerizations of α,ω-dicyanoalkanes were carried out in bulk at ambient temperature, the allylboration reactions took place instantly, but the molecular weights of the resulting polymers increased very slowly due to the slow dimerization of iminoborane species. The boron-containing polymers from trimethallylborane were found to be somewhat stable in comparison with those obtained from triallylborane.

In 5-3, allylboration polymerizations with allyldialkylboranes such as allyldi-*n*-hexylborane and di-*n*-hexylmethallylborane are described. The boron-containing polymers prepared from allyldialkylboranes were much stable in comparison with those prepared from triallyborane or trimethallylborane.

As an alternative method to obtain boron-containing polymers having boron-nitrogen four-membered rings, the condensation reactions of silylimines with substituted boranes such as chlorodialkylborane18) and methyl dialkylborinates are applied to the polymer synthesis (5-4, Scheme XIV). From the derivatives of di-*n*-alkylboranes and bis(silylimine)s derived from dialdehydes, polymers bearing boron-nitrogen four-membered structures in the main chain were produced.

Scheme XIV

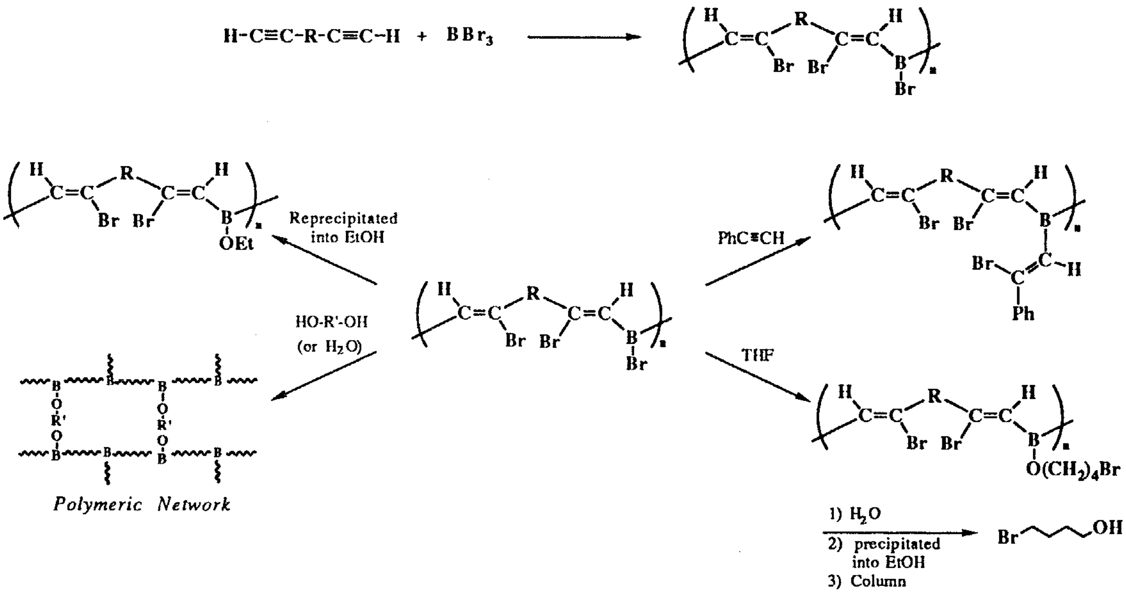


Chapter 6 Novel Boron-Containing Polymers and Related Reactions. For the further exploration of the methodology to obtain boron-containing polymers and for extending the methodology developed in the previous parts in this thesis, haloboration polymerization of diynes, hydroboration reaction of double bond-terminated polymers, dehydrogenation polymerization of monoalkylborane with diols, and a coupling polymerization of bifunctional organoboron compounds mediated with silver(I) are described.

In 6-1, a polyaddition reaction between boron tribromide and terminal diynes (i.e., "Haloboration Polymerization") is described as a novel methodology for the preparation of poly(organoboron halide)s having the unique character as poly(Lewis acid)s (Scheme

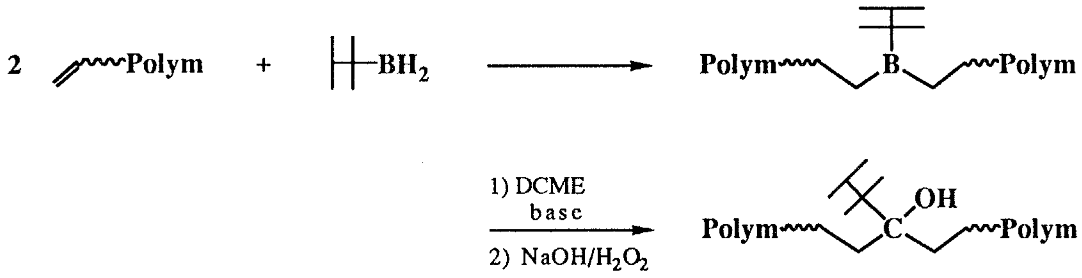
XV). For instance, a polyaddition between 1,7-octadiyne and boron tribromide produced a poly(organoboron halide) as a brown solid. This polymer was soluble in common organic solvents such as chloroform and dichloromethane. The structure of the polymer was supported by its spectroscopic analyses. The present haloboration polymerization was proved to proceed by *cis*- addition of B-Br to C≡C. During the precipitation of the polymer into ethanol, the B-Br moieties in the polymer were completely replaced to B-OEt. Similarly, the reaction of the polymer with diol or with H_2O produced the corresponding gel. The B-Br bond in the polymer was subjected to the further haloboration reaction with phenylacetylene. The characteristic property of the polymer as a poly(Lewis acid) was also demonstrated by the reaction with THF to produce 4-bromo-1-butanol after hydrolysis.

Scheme XV



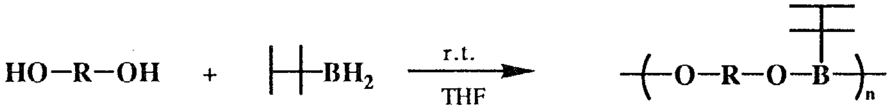
In 6-2, hydroboration reaction of double bond-terminated polymers with thexylborane to produce the polymer bearing one organoboron unit in the main chain is described (Scheme XVI). The molecular weight of the resulting polymer was duplicated in comparison with the starting polymer. The obtained polymer was subjected to the novel polymer reaction with α,α-dichloromethyl methyl ether (DCME). A polymer having one tertiary alcohol unit at the center of main chain was produced without obvious decrease of the molecular weight.

Scheme XVI



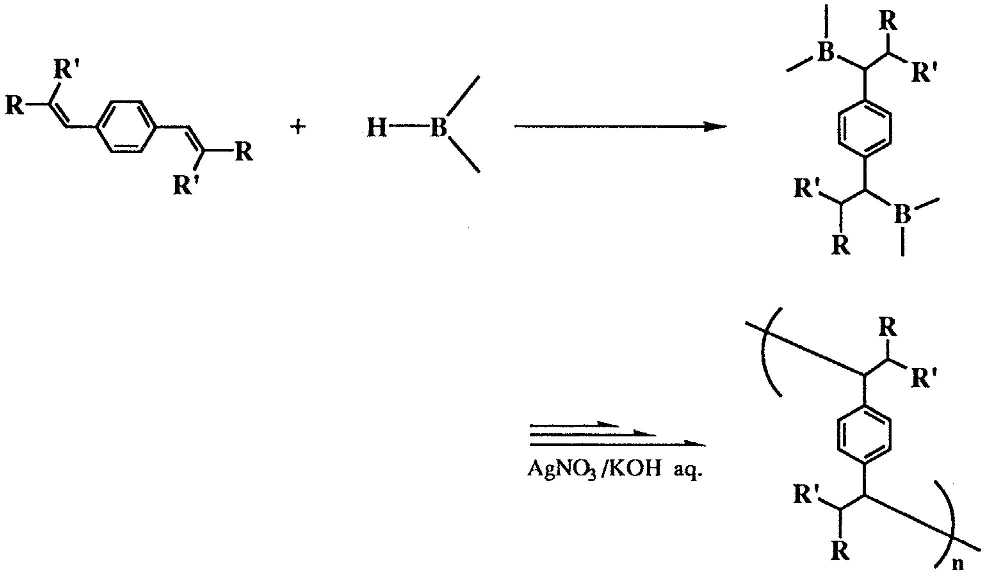
6-3 deals with the dehydrogenation reaction between thexylborane and diols to produce a novel boronate oligomer (Scheme XVII). When the reaction of thexylborane with an equimolar amount of 1,6-hexanediol was carried out at room temperature for 1 day, a colorless wax was obtained after removing the solvent. The cryoscopic measurement of the molecular weight of the obtained wax indicated the formation of oligomeric species. This oligomer was purified by coagulation with *n*-pentane, and characterized by spectroscopic analyses. The thermal stability of the resulting boronate oligomer is also described.

Scheme XVII



6-4 describes a novel polymerization by means of radical coupling reaction of telechelic organoboron compounds using silver(I) salt. Telechelic organoboron compounds were prepared by hydroboration of dienes and reacted with silver(I) nitrate under alkaline condition (Scheme XVIII). Organoboron compounds prepared from terminal dienes such as 1,7-octadiene or *p*-divinylbenzene gave only low molecular weights oligomeric coupling products due to the disproportionation of alkylsilvers or alkyl radicals. On the other hand, when dienes were designed as to favor the formation of benzylic boranes at hydroboration stage, the molecular weights of the corresponding polymers after coupling reactions were extremely higher in comparison with those of the polymers from terminal dienes.

Scheme XVIII



In this thesis, novel synthetic methodologies for the preparation of organoboron polymers are described together with various reactions starting from these polymers. The organoboron polymers themselves are expected as new polymeric materials having characteristic properties. In addition, these organoboron polymers can be used as polymeric precursors for functional polymers. In other words, a wide variety of functional groups can be introduced at the main chains, side chains, terminal ends, or even at the center of polymeric chains starting from these organoboron polymers. This type of polymer synthetic chemistry seems to have a high potential to provide functional polymers which are difficult to prepare by the known methods.

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Chapter 2

Hydroboration Polymerization

ABSTRACT

In this Chapter, polyaddition reaction of monoalkylborane, that is, "Hydroboration Polymerization" is described. In 2-1, diene monomers were used for the present polymerization system. The reaction of thexylborane with 1,7-octadiene was carried out in tetrahydrofuran at 0°C under nitrogen atmosphere to produce an organoboron polymer. The molecular weight of the polymer obtained increased as the feed ratio was approached to unity. As a diene component, 1,9-decadiene, *p*-divinylbenzene, *p*-diallylbenzene, bis(allyl ether)s of ethylene glycol, 1,4-butanediol, triethylene glycol, hydroquinone, and bisphenol A were used in this hydroboration polymerization to give the corresponding organoboron polymers. The thermal and oxidative stabilities of the obtained polymers were examined. These polymers were a little more stable toward air in comparison with conventional "trialkylboranes".

Synthesis of organoboron polymers by polyaddition between thexylborane and diynes is described in 2-2. When a terminal diyne was used as a monomer, a moderate amount of crosslinking reaction due to the second hydroboration towards vinylborane units in the main chain of the polymer took place. Even when an organoboron polymer was prepared from stoichiometric amount of two monomers, the obtained polymer showed only 60% of vinyl protons in its ^{1}H-NMR on the basis of an assumption of linear structure. That is, the resulting polymer had 20% of branched structure. As the result of crosslinking reaction, gelation was observed when an excess amount of borane was used. The gel obtained here, however, dissolved again by the treatment with methanol. On the other hand, when an internal diyne such as 3,9-dodecadiyne was used as a monomer, no gelation took place even in the presence of excess amount of thexylborane. Little contribution of branched structure was detected by the spectroscopic analyses of the polymer prepared from an equimolar amount of borane to diyne.

In 3-3, organoboron copolymers were prepared by the polyaddition between thexylborane and dienes mixture, or

diene/diyne mixture, respectively. When a mixture of dienes such as 1,2-diallyloxyethane and *p*-diallylbenzene was polymerized with thexylborane, the peaks in GPC using both UV and RI detectors were shifted to higher molecular weight regions with the increase of the amount of thexylborane. The molecular weight distribution of the polymer obtained by this method indicated clear difference from that of a mixture of two homopolymers. On the other hand, when the polymerization between thexylborane and 1,7-octadiene was carried out in the presence of a trace amount of 1,7-octadiyne, the molecular weights of organoboron polymers were found to be increased when the ratio of diyne to diene was increased.

1 - 1

Synthesis of Organoboron Polymers by the Polyaddition between Diene and Monoalkylborane.

Introduction

Hydroboration is a well-known methodology in organic synthesis, which takes place under mild conditions to produce various alkylborane compounds almost quantitatively. For these several decades, Brown *et al.* have established the chemistry of hydroboration1,2). However, the direct use of this reaction in polymer synthesis has been very limited so far. Among numerous studies reported by Brown and his group, the formation of polymeric materials has been described in their papers on the reaction of thexylborane and 1,3-butadiene3) or of monochloroborane and 1,7-octadiene4). However, no detail was reported about the yield, molecular weights, and characterization (structure) of the resulting polymers. These polymers were formed as intermediates to obtain boron heterocycles by the so-called "thermal depolymerization".

Previously, Urry *et al.* mentioned that the organoboron polymer was formed by the pyrolysis of 2,5-dimethyl-2,5-diborahexane5). Mikhailov *et al.* also reported the formation of organoboron polymer by thermal isomerization of triallylborane and triisobutylborane6). However, these reactions required severe conditions, and the obtained polymers have not been characterized. Recently, Pinazzi has described the modification of polybutadiene by the hydroboration method7). Chung also reported the polymers having organoboron branches for the preparation of polymers with alcohol functionalities8-10).

In this section, polyaddition between diene and monoalkylborane (i.e., "Hydroboration Polymerization") is described. This is the first example to study the nature of polymerization and to characterize the structure and the molecular weight of organoboron polymers. The resulting organoboron polymer can be regarded as a polymer homologue of trialkylborane and can be used as a novel type of polymer having unique reactivities and properties.

Results and Discussion

According to the previous reports, some monoalkylboranes such as thexylborane[11], (S-B) 3-(methylthio)propylborane[12], and monoalkylborane-amine complexes[13] are known to be stable enough as bifunctional B-H compounds. Among them, thexylborane (**1**) is gradually decomposed in a THF solution.[11] However, **1** is found to be stable enough after distillation (in the bulk)[14]. Thus, the distilled **1** was employed as a bifunctional monoalkylborane component in the present hydroboration polymerization. In reference to the previous studies, the cyclized products were formed by the reactions of **1** with 1,3-butadiene,[3] 1,4-pentadiene[3], 1,5-hexadiene[3], diallylamines[15], divinylsilanes[16], diallylsilanes[16], and so on. To avoid this competitive cyclization reaction, relatively longer chain dienes were used here.

The reaction condition in this study was fixed at the temperature of 0°C, and a monomer was added to a 1.0M THF solution of another monomer by using a microfeeder. Similarly to the conventional "trialkylboranes", the organoboron polymer may be unstable under air. This instability requires the careful GPC measurement to avoid the decomposition of the obtained organoboron polymers. Thus, GPC analysis should be carried out by using air- and peroxide-free THF as an eluent. In addition, continuous nitrogen bubbling in THF during the analysis made in success of the measurement of the molecular weights of organoboron polymers.

Dependence of Molecular Weight on the Feed Ratio of Monomers. Generally, the stoichiometry of the employed two monomers is quite important in polyaddition reaction. Thus, the dependence of the feed ratio of monomers was examined in the hydroboration polymerization between thexylborane (**1**) and 1,7-octadiene (**2a**). When **1** was added to a THF solution of **2a** (method A), the molecular weight of the polymer obtained increased with the approach of the feed ratio to unity (Table I, Figure 1).

Table I Dependence of M.W. on the Feed Ratio of 1/2a a).

Run	1 (mmol)	2a (mmol)	1/2a	$\overline{M}_n$ b)	$\overline{M}_w$ b)
1	0.64	0.95	0.68	540	840
2	0.73	0.96	0.76	850	1,710
3	0.91	0.93	0.98	1,770	6,540
4	0.98	0.92	1.05	19,000	27,700
5	1.10	0.98	1.12	18,000	27,000
6	1.11	0.92	1.22	14,000	21,600
7	1.24	0.98	1.27	11,900	19,100
8	1.43	1.01	1.42	13,300	21,800

a) Reactions were carried out by adding 1 to a THF 1M solution of 2a using a microfeeder at 0°C under nitrogen.

b) GPC (dry THF), polystyrene standard.

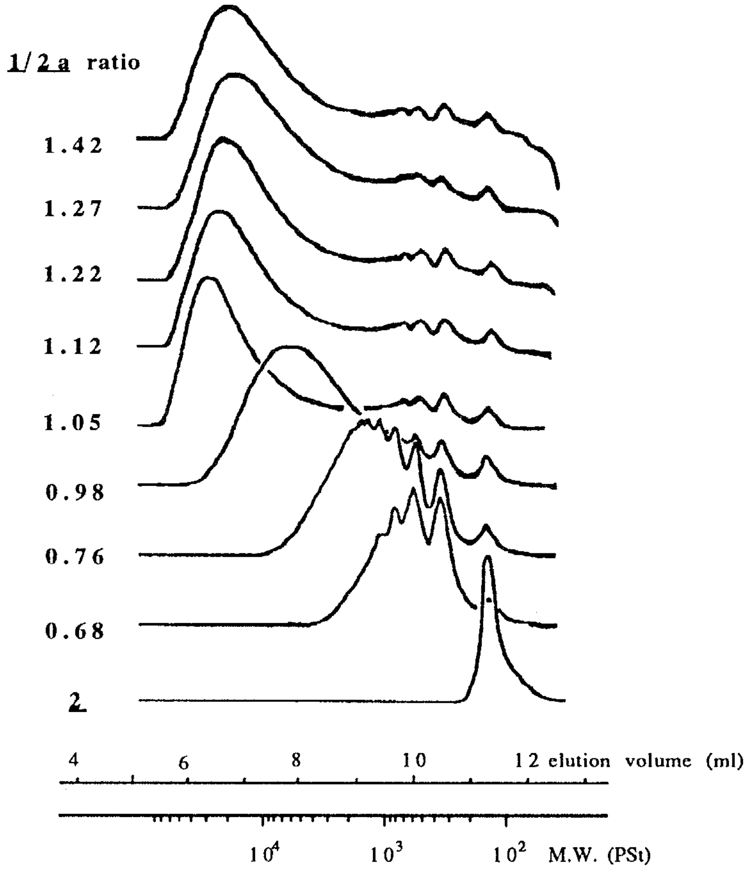


Figure 1 GPC traces of the product polymers in hydroboration polymerization by changing the feed ratio of 1 to 2a.

Table II Dependence of M.W. on the Feed Ratio of 2a/1[a].

Run	1 (mmol)	2a (mmol)	2a/1	$\overline{M}_n$[b]	$\overline{M}_w$[b]
1	1.00	0.63	0.63	940	2,270
2	1.05	0.77	0.73	1,150	3,040
3	1.03	0.92	0.89	2,830	8,910
4	1.00	0.98	0.98	3,470	12,200
5	0.97	1.02	1.05	4,370	14,600
6	0.98	1.19	1.21	2,900	14,000
7	0.97	1.29	1.33	1,850	13,400

a) Reactions were carried out by adding 2a to a THF 1M solution of 1 using a microfeeder at 0°C under nitrogen.

b) GPC (dry THF), polystyrene standard.

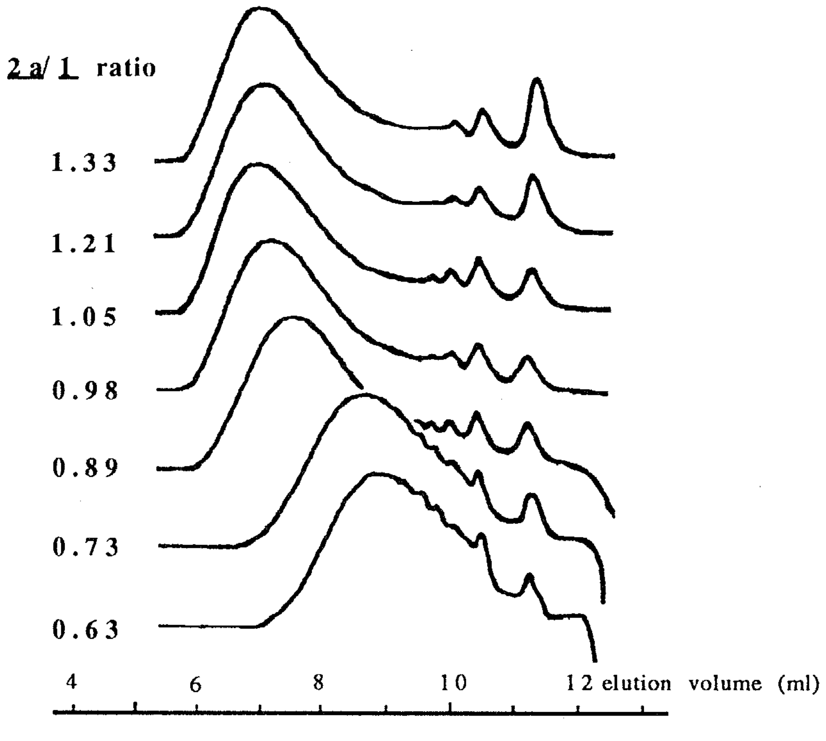


Figure 2 GPC traces of the product polymers in hydroboration polymerization by changing the feed ratio of 2a to 1.

The number-average molecular weight of the polymer obtained was up to 19,000 from the result of GPC using polystyrene calibration curves.[17] The rate of the addition of 1 was 10μmol/min. In the case of fast addition (400μmol/min.) of 1, no change of the molecular weight was observed. This result shows that the polymerization was completed during the addition of the monomer. In other words, an excess amount of **1** remained when the feed ratio was higher than unity. Accordingly, the decrease of molecular weight in this case might be caused by the so-called back-biting reaction (disproportionation between the polymer chain and **1**)[18]. This is not clear at the present time because the contribution of this reaction should be too small to be detected. However, it is confirmed at least that the molecular weight reached a maximum when the feed ratio of two monomers came to unity or slight excess.

Another method, in which **2a** was added to a THF solution of **1** (method B), also showed similar results and is summarized in Table II and in Figure 2. The molecular weight of the obtained polymer was increased when the feed ratio reached unity. Thus, method A was used for hydroboration polymerization of various dienes. In all cases, a slight excess of **1** was employed.

Hydroboration Polymerization of Various Dienes. The general scheme of hydroboration polymerization is shown in Scheme I. Similarly to **2a**, various hydrocarbon diolefins such as 1,9-decadiene (**2b**), *p*-divinylbenzene (**2c**), and *p*-diallylbenzene (**2d**) were used for this polymerization. Diolefins containing oxygen atoms (**2e**-**2i**) also produced the corresponding organoboron polymers. In all cases, the obtained polymers were colorless gum and soluble in common organic solvents such as THF, chloroform, and benzene. These results are summarized in Table III. The molecular weights of the polymers from ethers were somewhat lower than those from hydrocarbon olefins. This might be the result of intramolecular coordination of an oxygen atom to boron.

Scheme I

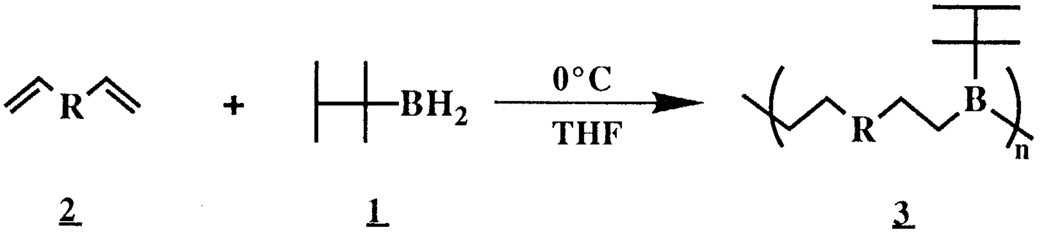
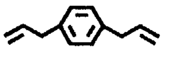
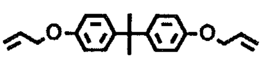


Table III Hydroboration Polymerization between Thexylborane and Various Dienes[a)]

Run	Diene		$\overline{M}_n$[b)]	$\overline{M}_w$[b)]
1		(2a)	19,000	27,700
2		(2b)	18,400	27,400
3		(2c)	19,000	29,200
4		(2d)	9,400	16,900
5		(2e)	1,200	2,600
6		(2f)	1,900	4,500
7		(2g)	1,900	3,200
8		(2h)	5,100	11,200
9		(2i)	7,600	15,400

a) Polymerizations were carried out by adding small excess of thexylborane to the 1M THF solution of diene at 0°C.

b) GPC (dry THF), polystyrene standard.

Stability of Organoboron Polymer. The organoboron polymers obtained by hydroboration polymerization were stable enough against protic solvents such as water and alcohol under nitrogen.[2)] However, under air, these polymers were unstable as usual for organoboron compounds[19,20)]. This decomposition was monitored by GPC after the air bubbling in THF solution of **3a** at room temperature. The results are illustrated in Figure 3. After 3min. of air-bubbling, the peak became broader and moved to the low molecular weight region. At 30 min., the molecular weight decreased to almost several hundreds. However, in comparison with conventional "trialkylboranes", it should be noted here that the present organoboron polymer was a little more stable toward air.

A THF solution of organoboron polymer (**3a**) was refluxed under nitrogen to form a gel. This gelation might be caused by hydroborane (B-H) species, which were turned by thermal β-elimination (*retro*-hydroboration) of the thexylborane group to evolve 2,3-dimethyl-2-butene. It can be considered that the hydroboration reaction of this B-H group with the terminal double bond in the polymer produced a boron-containing gel.

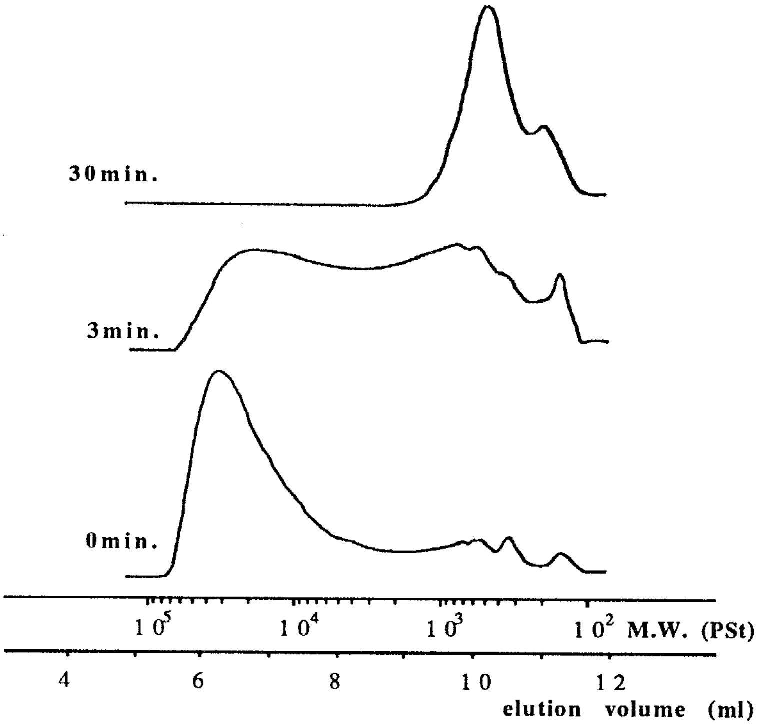


Figure 3 GPC traces of **3a** (0min.), the product after 3min. air-bubbling in THF solution of **3a** (3min.), and the product after 30min. air-bubbling (30min.).

From the results of thermogravimetric analysis of **3a** (Figure 4), the weight loss of the polymer started at 190°C and completed at 480°C under a nitrogen stream. On the other hand, under air, **3a** began to lose its weight at 110°C. The weight was kept to be nearly 10% above 450°C. After thermal analysis, a black solid remained in a cell under air.

The polymers obtained in the present hydroboration polymerization have a structure consisting of C-B bonds in the main chain. Generally, these organoboron polymers can be regarded as a polymer homologue of trialkylborane, which is known to be a very versatile compound in organic synthesis. Thus, the polymers obtained by hydroboration polymerization can be expected as a novel type of reactive polymers, which will be demonstrated in the next part of this thesis.

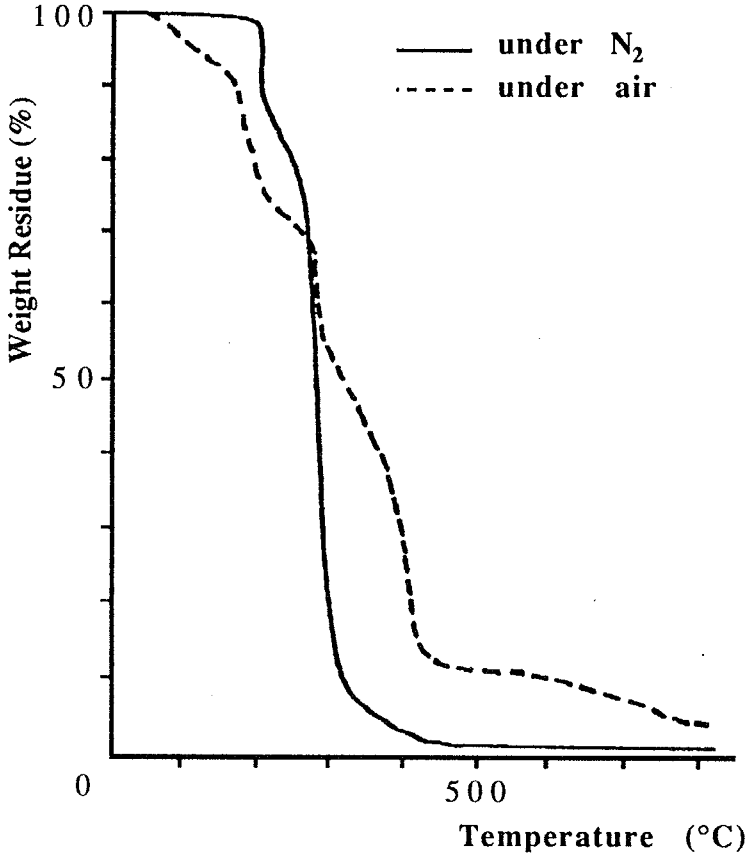


Figure 4 TGA (10°C/min.) traces of 3a under nitrogen or under air.

Experimental Section

Materials and Instruments. Borane-tetrahydrofuran (THF) complex and borane-dimethyl sulfide were obtained from Merck Co. 2,3-Dimethyl-2-butene, allyl bromide, 1,7-octadiene, 1,9-decadiene, *p*-divinylbenzene, and all solvents were dried and distilled under nitrogen. Various diols were purified by distillation or by recrystallization. Thexylborane (1,1,2-trimethylpropylborane) (**1**) was prepared by the reaction of borane-THF complex3) or of borane-dimethyl sulfide21) with 2,3-dimethyl-2-butene as reported earlier and was purified by distillation [48-49°C (0.1 mmHg)]. Hydrogen titration by hydrolysis of **1** showed that the isolated sample was pure enough for the following hydroboration polymerization.

IR spectra were obtained on a Hitachi 260-50 grating spectrophotometer. ^{1}H-NMR spectra were recorded in $CDCl_3$ on a Hitachi R-600 (60MHz) instrument. Gas chromatographic analysis (GC) was made on a Shimadzu GC-6A instrument. Gel permeation chromatographic analysis (GPC) was carried out on a Tosoh HLC-8020 (TSK gel G3000) by using dried THF as an eluent with nitrogen bubbling after calibration with standard polystyrene samples. Thermogravimetric analysis (TGA) was made on a Shimadzu DT-30 instrument (15°C/min.) under an air or a nitrogen stream. Cryoscopic experiment was carried out under nitrogen atmosphere by using benzene as a solvent.

Synthesis of *p*-Diallylbenzene (2d). To a benzene solution of *p*-dibromobenzene (7.94g, 33.7mmol) and $PdCl_2(PPh_3)_2$ (0.45g, 0.64mmol) were added allyltributyltin (0.48g, 1.45mmol) and a THF solution of allylmagnesium chloride (1.0M, 80mL) under nitrogen. The mixture was stirred for 1 day at a reflux temperature. The obtained **2d** was purified by SiO_2 column chromatography (*n*-hexane) and then by distillation. Yield: 1.58g (9.98 mmol, 30%).

Bis(allyl ether)s of Ethylene Glycol (2e), 1,4-Butanediol (2f), and Triethylene Glycol (2g). To a 100mL THF suspension of *n*-hexane-washed sodium hydride (4.3g, 180mmol) were added ethylene glycol (5.6g, 90mmol) and then allyl bromide (22g, 180mmol) slowly at 0°C. After 1 day refluxing, 100mL of water was added to the reaction mixture. The organic layer was extracted with three portions (100mL) of diethyl ether and dried over magnesium sulfate. After evaporation of solvent, **2e** was dried over sodium and distilled [72-73°C (26mmHg)]. Yield: 6.5g (46mmol, 51%). **2f** and **2g** were obtained similarly in 67% [83-84°C (10mmHg)] and 56% [108-110°C (0.65mmHg)] yield, respectively.

Bis(allyl ether)s of Hydroquinone (2h) and Bisphenol A (2i). To a 40mL acetone suspension of potassium carbonate (5.5g, 40mmol) were added hydroquinone (2.3g, 21mmol) and allyl bromide (5.6g, 46mmol) at ambient temperature. After refluxing for 15h, 50mL of diluted aqueous sodium hydroxide was added to the reaction mixture. The organic layer was extracted with three portions (100mL) of diethyl ether and dried over magnesium sulfate. The purification with SiO_2 column chromatography (*n*-hexane) gave 3.6 g (19mmol, 90%) of **2h** as a white crystal (mp 31.9-32.4°C). In a similar manner, **2i** was obtained as a colorless oil in 81% yield.

Polyaddition between 1,7-Octadiene (2a) and Thexylborane (1). The dependence of the molecular weight of the polymer obtained on the feed ratio was examined as follows. **1** was added slowly (45μmol/min.) to a 1.0M THF solution of **2a** by using a microfeeder at 0°C under nitrogen. After 1h stirring at 0°C, GPC analysis was subjected directly. Amounts of **1** and **2a** used are summarized in Table I. On the other hand, **2a** was added slowly (40μmol/min.) to a THF solution of **1** by a procedure similar to that described above. These experiments are summarized in Table II.

As a typical example of the polymerization, **1** (0.096g, 0.98mmol) was added to a 1.0M THF solution of **2a** (0.102g, 0.92mmol) by using a microfeeder (45μmol/min.) at 0°C under nitrogen. The evaporation of solvent gave a colorless gum in a quantitative yield. The obtained organoboron polymer (**3a**) was soluble in common organic solvents such as THF, chloroform, benzene, and *n*-hexane. All the spectroscopic analyses and GPC measurements were performed without further purification. **3a**: ^{1}H-NMR (δ, ppm) 0.52-1.02 ($-CH_3$, 12H), 1.02-2.20 (-CH, $-CH_2-$, 17H); IR (neat) 2940, 1470cm^{-1}. **3a** can be further purified by reprecipitation from THF into dried DMF under nitrogen and isolated in 64% yield.

Hydroboration Polymerizations of Various Dienes with 1. The following organoboron polymers were obtained in quantitative yields by using a procedure similar to that described for **3a**. **3b** from **1** (0.091g, 0.93mmol) and **2b** (0.109g, 0.79mmol): ^{1}H-NMR (δ, ppm) 0.58-1.02 ($-CH_3$, 12H), 1.02-2.20 (-CH, $-CH_2-$, 21H); IR (in $CHCl_3$) 2840, 1460, 1350cm^{-1}. **3c** from **1** (0.095g, 0.96mmol) and **2c** (0.117g, 0.90mmol): ^{1}H-NMR (δ, ppm) 0.54-1.02 ($-CH_3$, 12H) 1.09-2.04 (-CH, $-CH_2-$, 5H), 2.35-2.98 ($ArCH_2-$, 4H), 7.14 (C_6H_4, s, 4H); IR (in $CHCl_3$) 2960, 1455, 1340cm^{-1}. **3d** from **1** (0.097g, 0.99mmol) and **2d** (0.136g, 0.86mmol): ^{1}H-NMR (δ, ppm) 0.49-0.92

($-CH_3$, 12H), 1.02-2.21 ($-CH$, $-CH_2-$, 9H), 2.60 ($ArCH_2-$, m, 4H), 7.10 (C_6H_4, s, 4H); IR (in $CHCl_3$) 2950, 1512, 1458cm^{-1}. **3e** from **1** (0.116g, 1.19mmol) and **2e** (0.154g, 1.08mmol): ^{1}H-NMR (δ, ppm) 0.58-1.03 ($-CH_3$, 12H), 1.03-2.12 ($-CH$, $-CH_2-$, 9H), 3.28-3.91 (OCH_2-, 8H); IR (neat) 2940, 1465, 1320, 1100cm^{-1}. **3f** from **1** (0.099g, 1.01mmol) and **2f** (0.160g, 0.94mmol): ^{1}H-NMR (δ, ppm) 0.53-0.98 ($-CH_3$, 12H), 0.98-2.36 ($-CH$, $-CH_2-$, 13H), 3.13-3.66 (OCH_2-, 8H); IR (in $CHCl_3$) 2950, 1466, 1366, 1244, 1103cm^{-1}. **3g** from **1** (0.113g, 1.15mmol) and **2g** (0.237g, 1.03mmol): ^{1}H-NMR (δ, ppm) 0.55-1.12 ($-CH_3$, 12H), 1.12-2.21 ($-CH$, $-CH_2-$, 9H), 3.24-4.16 (OCH_2-, 16H); IR (neat) 2950, 1460, 1360, 1085cm^{-1}. **3h** from **1** (0.108g, 1.11mmol) and **2h** (0.182g, 0.95mmol): ^{1}H-NMR (δ, ppm) 0.53-1.02 ($-CH_3$, 12H), 1.02-2.40 ($-CH$, $-CH_2-$, 9H), 3.89 (OCH_2-, m, 4H), 6.81 (C_6H_4, s, 4H); IR (in $CHCl_3$) 2957, 1505, 1468, 1238, 1061, 1030, 826cm^{-1}. **3i** from **1** (0.089g, 0.91mmol) and **2i** (0.247g, 0.78mmol): ^{1}H-NMR (δ, ppm) 0.62-1.05 ($-CH_3$, 12H), 1.08-2.46 ($-CH$, $-CH_2-$, $-CH_3$, 15H), 3.60-4.35 (OCH_2-, m, 4H), 6.62-7.34 (C_6H_4, m, 8H); IR (in $CHCl_3$) 2959, 1608, 1510, 1469, 1248, 1011, 832cm^{-1}.

Stability of Organoboron Polymer 3a toward Air. The oxidation stability of **3a** toward air was examined by monitoring the change of the GPC curve during an oxidation experiment, in which a stream of air was bubbled (at a rate of 120mL/min.) into a THF (1mL) solution of **3a** (0.26g). After the designated time, the resulting polymer was characterized by GPC analysis.

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14) Even after 3 months, hydrogen titration and oxidation reaction (to produce thexyl alcohol quantitatively) supported no change of thexylborane. 2,3-Dimethyl-1-butanol as an isomerized product was also not detected by GC after oxidation of thexylborane.

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17) Cryoscopic analysis showed that the molecular weight of **3a** (Table I, run 4) was higher than 6,000, which also supported the formation of polymeric material in the present reaction.

18) This reaction is commonly accepted for diborane; see for example: Brown, H. C.; Negishi, E.; Bucket P. L. *J. Am. Chem. Soc.*, **1970**, 92, 6649. The reaction for monochloroborane is also supposed in a similar manner (ref. 4).

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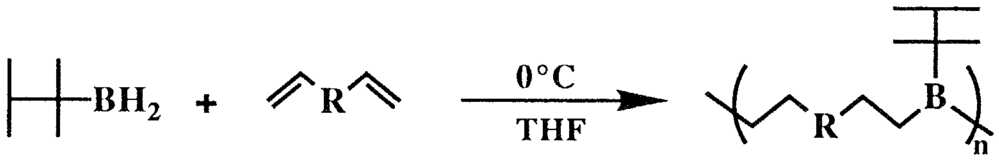
2 - 2

Synthesis of Organoboron Polymers by the Polyaddition between Diyne and Thexylborane.

Introduction

Synthesis of polymeric organoboron compounds has been an attractive target for the preparation of new materials and reactive intermediates producing functional polymers. However, there have been very few examples dealing with their synthetic works. In the previous section, the author has described the synthesis of organoboron polymers by a novel polyaddition reaction between diene and thexylborane (**1**) (i.e., "Hydroboration Polymerization", Scheme I).

Scheme I



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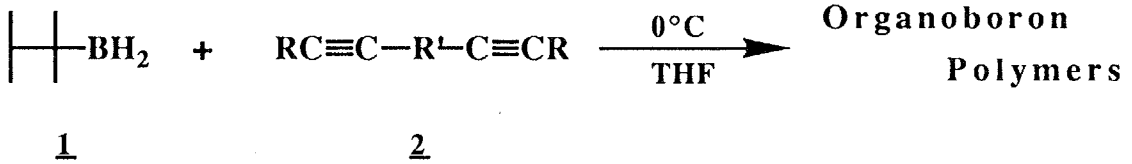
Since polymers prepared by hydroboration polymerization can be regarded as a polymer homologue of trialkylborane, these polymers are expected to show similar reactivities as those of conventional organoboron compounds, which will be described in the following chapter of this thesis. If diyne compounds are used in the present polymerization system, the structure of the resulting polymers should be quite different from those from dienes, because the reactivity towards hydroboration itself is known to be different. As a result, polymerization behavior as well as the properties for materials and the reactivities of the polymers might be expected to be different. In this chapter, hydroboration polymerization between diyne compounds (**2**) and thexylborane (**1**) to produce novel organoboron polymers is described.

Results and Discussion

According to a previous report¹⁾, acetylenes are reactive towards hydroboration reaction as well as olefins. The reactivity of terminal acetylene towards hydroboration is quite different from that of internal acetylene. That is, the terminal acetylenes preferentially give dihydroboration products *via* a further hydroboration of the initially formed vinylborane species, when the borane components are not sterically hindered. If a borane is bulky like disiamylborane²⁾, however, the monohydroboration products are predominantly produced. On the other hand, the internal acetylenes give monohydroboration products regardless of the bulkiness of borane reacted. In this section, both terminal and internal diynes were examined respectively for the hydroboration polymerization with bifunctional thexylborane (**1**) (Scheme II).



	R	R'
2a;	H,	$-(CH_2)_4-$
2b;	Et,	$-(CH_2)_4-$
2c;	Et,	$-(CH_2)_3-$
2d;	Et,	$-(CH_2)_5-$
2e;	Me,	$-(CH_2)_4-$

Scheme II

Hydroboration Polymerization between 1 and Terminal Diyne. As a preliminary experiment, 1,7-octadiyne (**2a**) was used as a terminal diyne component, and the hydroboration polymerization with various amounts of **1** was examined. The reaction was carried out by adding **1** to a THF solution of **2a** at 0°C using a microfeeder³⁾. Results of GPC measurements (dried THF as an eluent with constant nitrogen bubbling⁴⁾) are summarized in Figure 1 and Table I. When the feed ratio of **1** to **2a** approached to unity, the molecular weight of the obtained polymer was increased as was usual for the step-growth polymerization. Over unity, however, gelation was observed in every feeding ratio.

Table I Dependence of Molecular Weight on the Feed Ratio of 1/2a.[a]

Run	2a g(mmol)	1 g(mmol)	1/2a ratio	$\overline{M}_n$[b]	$\overline{M}_w$[b]
1	0.089 (0.84)	0.057 (0.59)	0.70	750	1,140
2	0.092 (0.87)	0.065 (0.66)	0.77	930	1,540
3	0.057 (0.54)	0.047 (0.48)	0.90	1,120	2,610
4	0.080 (0.75)	0.070 (0.71)	0.95	1,210	2,960
5	0.081 (0.77)	0.079 (0.80)	1.04	-[c,d]	-[c,d]
6	0.090 (0.85)	0.098 (1.00)	1.17	2,330[c]	13,900[c]
7	0.066 (0.62)	0.094 (0.95)	1.54	1,460[c]	4,240[c]
8	0.061 (0.58)	0.097 (0.99)	1.72	1,230[c]	2,680[c]

a) Reactions were carried out by adding 1 to a 1.0M THF solution of 2a using a microfeeder (45μmol/min).
b) GPC (dried THF), polystyrene standard.
c) These systems initially formed the corresponding gels, which dissolved by the treatment with MeOH.
d) The molecular weight was higher than the excluded volume (>6x10^4).

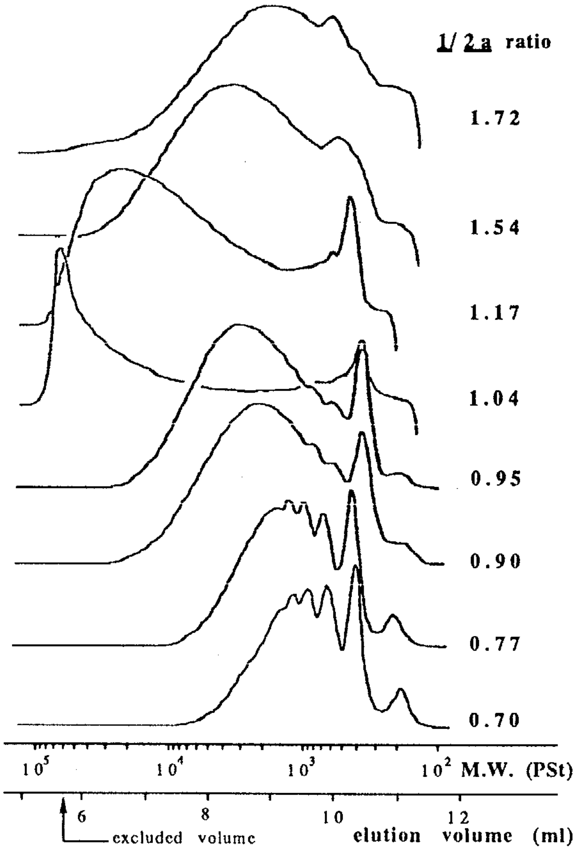
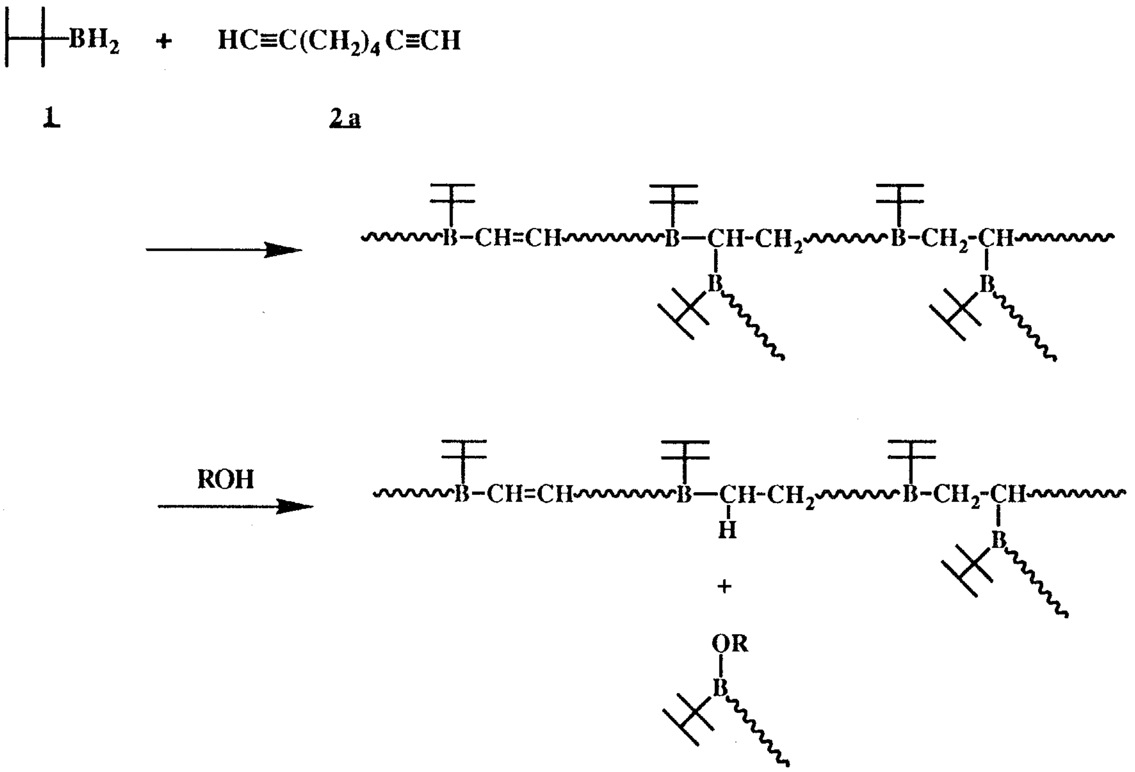


Figure 1 Dependence of molecular weight of 3a on the feed ratio of the monomer (1/2a).

Interestingly, all the gels became soluble after the treatment with alcohols such as methanol or ethanol. Thus, GPC measurements were performed after alcoholysis. Generally, alkylborane or alkenylborane is not reactive against the alcoholic protons, while C-B bonds in alkenylboranes are known to be cleaved by alcohols under the severe condition[5]. However, the carbon atom having two C-B bonds (i.e., *gem*-diboramethynes) were reported to be cleaved quite easily under protic conditions[6]. Therefore, the gel should be cleaved at the *gem*-diboramethyne units in the main chain of the polymer (Scheme III).

Scheme III



The tendency of lowering the molecular weight by using an excess amount of **1** might be also explained in a similar way. That is, excess of **1** should result in the increase of the proportion of *gem*-diboramethyne units as well as that of 1,2-diboraethylene units in the main chain of the polymer. The former units are readily broken by the treatment with alcohol to form soluble polymer. Accordingly, the increase of this structure in the main chain resulted in the decrease of molecular weight of the polymer after alcoholysis.

In the ^{1}H-NMR spectrum of the polymer obtained with an equivalent amount of **1**, vinyl protons were observed only in 60% on the basis of an assumption of the linear structure (i.e., monohydroboration product). Therefore, it may be concluded that the polymerization with terminal acetylene resulted in the formation of highly branched structure in the polymer chain.

Hydroboration Polymerization between 1 and Internal Diyne. Similarly to the case of **2a** and **1**, polymerizations were carried out in several feeding ratios of **1** and 3,9-dodecadiyne (**2b**). As shown in Figure 2 and Table II, the polymer peaks in GPC shifted to a higher molecular weight region when the feed ratio of **1** to **2b** was increased. Over unity, however, the molecular weight of the resulting polymer (**3b**) did not increase in sharp contrast to terminal diyne. This dependence on feed ratio was quite similar to the hydroboration polymerization of dienes7). If monomers were added in an opposite way, i.e., **2b** was added to a THF solution of **1**, the resulting polymer showed a lower molecular weight (M_n=460, M_w=2,940). The decrease of molecular weight at the feed ratios over unity and in the case of opposite monomer feeding may be due to a back biting reaction by the disproportionation between **1** and polymer chains as was discussed in the previous chapter.

Table II Dependence of Molecular Weight on the Feed Ratio of 1/2b.a)

Run	2b g(mmol)	1 g(mmol)	1/2b ratio	M_n b)	M_w b)
1	0.094 (0.58)	0.036 (0.37)	0.63	560	860
2	0.121 (0.74)	0.065 (0.67)	0.90	790	1,980
3	0.053 (0.32)	0.033 (0.33)	1.03	1,410	13,900
4	0.099 (0.61)	0.067 (0.69)	1.12	1,190	11,800
5	0.090 (0.56)	0.082 (0.84)	1.50	1,130	8,920

a) Reactions were carried out by adding 1 to a 1.0M THF solution of 2b using a microfeeder (45μmol/min).

b) GPC (dried THF), polystyrene standard.

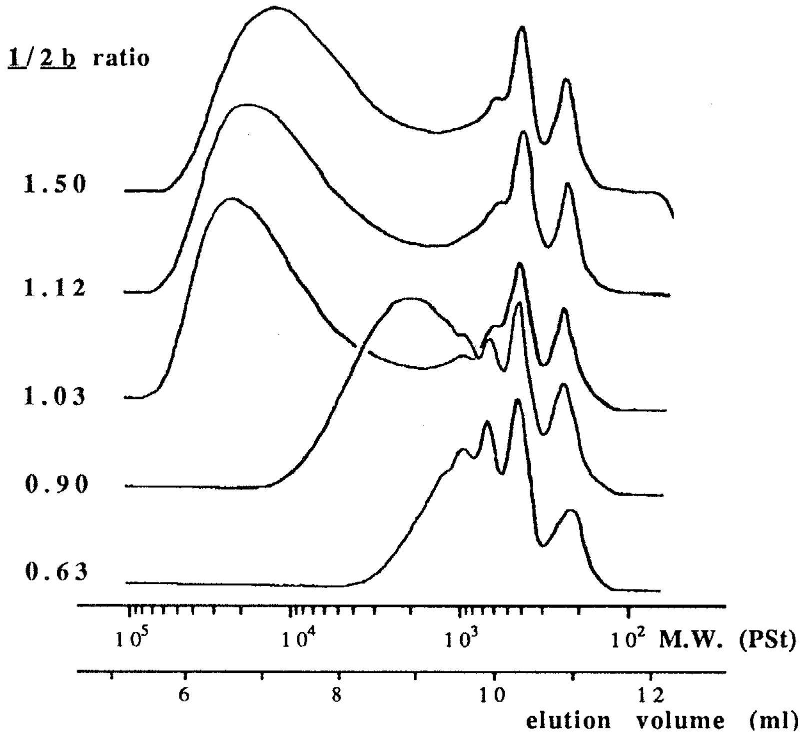


Figure 2 Dependence of molecular weight of 3b on the feed ratio of the monomer (1/2b).

In the ^{1}H-NMR spectrum of the polymer (**3b**) obtained with an equimolar amount of **1**, more than 90% of vinyl protons on the assumption of the linear structure were observed. These results are taken to indicate that the hydroboration polymerization of internal diynes with **1** takes place in a similar way to that of dienes, because the vinylboranes formed by monohydroboration almost remained unreacted in this polymerization.

Table III Hydroboration Polymerization of Various Internal Diynes.[a)]

Run	Diyne (2)		1/2 ratio	M_n[b)]	M_w[b)]
1	$EtC\equiv C(CH_2)_3C\equiv CEt$	(2c)	1.07	570	5,300
2	$EtC\equiv C(CH_2)_4C\equiv CEt$	(2b)	1.03	1,410	13,900
3	$EtC\equiv C(CH_2)_5C\equiv CEt$	(2d)	1.12	2,080	17,900
4	$MeC\equiv C(CH_2)_4C\equiv CMe$	(2e)	1.06	1,030	10,640

a) Reactions were carried out by adding 1 to a 1.0M THF solution of 2 using a microfeeder (45μmol/min).

b) GPC (dried THF), polystyrene standard.

As mentioned above, due to the poor reactivity of alkenylborane unit prepared from internal diyne towards hydroboration, gelation can be avoided. Other internal diynes were also examined for hydroboration polymerization by using a small excess amount of **1**. The results are summarized in Table III. 3,8-Undecadiyne (**2c**), 3,10-tridecadiyne (**2d**), 2,8-decadiyne (**2e**) as well as 3,9-dodecadiyne (**2b**) produced the corresponding organoboron polymers.

Stability of Organoboron Polymer (3b). Thermal stability of **3b** was examined by TGA measurement under nitrogen and under air (Figure 3). Under nitrogen, the weight loss started at 100°C, and was completed at 500°C. Under air, a larger amount of residue was remained after pyrolysis in comparison with that under nitrogen. Organoboron polymer (**3b**) was rather unstable under air (*vide infra*). Thus, oxidation (i.e., decomposition of the polymer) should competitively take place during the measurement of TGA under air.

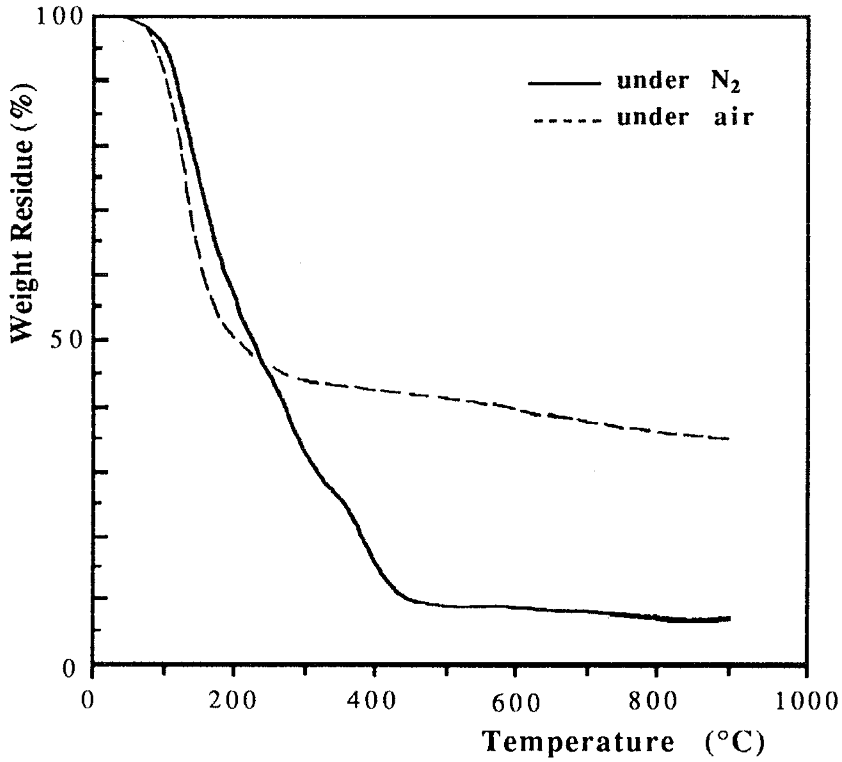


Figure 3 Results of TGA measurement of **3b** under nitrogen and under air.

Air stability of **3b** was monitored by checking the change of molecular weights in GPC after the air bubbling of THF solution of **3b** (Figure 4). Throughout the air bubbling, the molecular weight of **3b** decreased to several hundreds. As the decomposition of the polymer proceeded, the intensity of UV detector in GPC was decreased. Vinylboranes are known to have strong UV absorptions8). Thus, the decrease of intensity of UV can be attributed to the decomposition of this structure in the polymer chains. From the IR spectrum of the sample after 1h, a strong carbonyl peak at $1710\mathrm{cm}^{-1}$ was observed. This should be the result of the oxidation of vinylborane moieties to form the corresponding ketones.

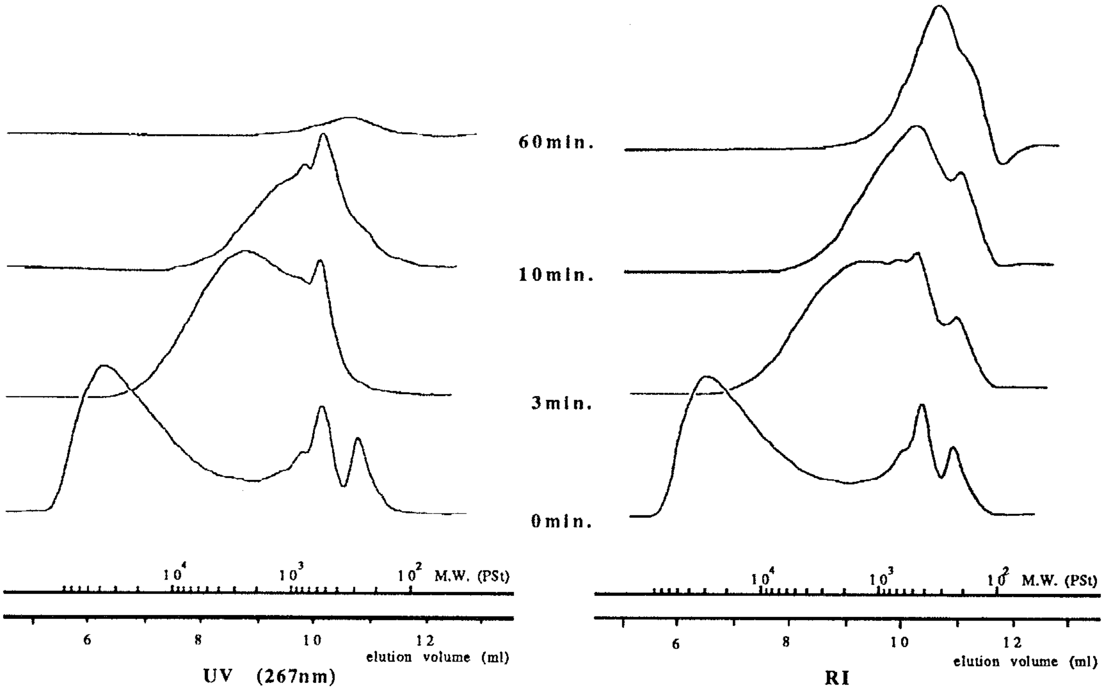


Figure 4 GPC traces of air decomposition of 3b.

As these polymers consist mainly of divinylborane units, the different reactivity and stability originated from this structure can be expected in comparison with the organoboron polymers prepared from dienes and **1**. The reactions of these poly(divinylborane)s prepared here may provide a useful synthetic methodology to obtain novel functional polymers.

Experimental Section

Materials and Instruments. **1** was prepared by the reaction of borane-dimethyl sulfide and 2,3-dimethyl-2-butene as reported earlier$^{9)}$, and was purified by distillation$^{7)}$. Tetrahydrofuran was dried over lithium aluminum hydride and distilled before use. **2a**-**2e** were purified by distillation.

^{1}H-NMR spectrum was recorded in $CDCl_3$ on a Hitachi R-600 instrument (tetramethylsilane as an internal standard). IR spectrum was obtained on a Perkin Elmer 1600 spectrometer. Gel permeation chromatographic analysis was carried out on a Tosoh HLC-8020 (TSK gel G3000) by using dried THF as an eluent with constant nitrogen bubbling after calibration with standard polystyrene samples. Thermogravimetric analysis (TGA) was made on a Shimadzu DT-30 instrument (15°C/min.) under air or nitrogen stream.

Hydroboration Polymerization between 1 and 1,7-Octadiyne (2a). A general procedure for the polymerization between **1** and **2a** is described as follows: To a 1.0M THF solution of **2a**, **1** was added by using a microfeeder (45μmol/min.) at 0°C under nitrogen. The reaction mixture was stirred for 1h at that temperature. GPC measurement was performed as described in R&D section. When excess **1** was used for this polymerization, a gelation was observed. The obtained gel was dissolved by the treatment with ethanol (0.1ml) and the resulting solution was subjected to the GPC measurement. The ratios between **1** and **2a** are listed in Table I. **3a** after methanolysis (Table I, run 5); ^{1}H-NMR (δ, ppm) 0.53-2.56 ($-CH_3$), 1.10-2.56 ($-CH_2$, -CH), 6.32 (C=C-H); IR (in $CHCl_3$) 2952, 2866, 1610, 1462, 1433, 1372, 1289, 1150, 999, 913cm^{-1}.

Hydroboration Polymerization between 1 and Internal Diyne (2b) (Stoichiometric Studies). A general procedure for the polymerization between **1** and **2b** is described as follows: To a 1.0M THF solution of **2b**, **1** was added by using a microfeeder (45μmol/min.) at 0°C under nitrogen. The reaction mixture was stirred for 1h at that temperature. GPC measurement was performed as described in R&D section. The ratios between **1**

and **2b** are listed in Table II. **3b** (Table II, run 4); ^{1}H-NMR (δ, ppm) 0.49-1.17 (-CH_3), 1.17-2.52 (-CH_2, -CH), 5.14-5.98 (C=C-H); IR (in $CHCl_3$) 2959, 2869, 1567, 1462, 1373, 1211, 1049, 850cm^{-1}.

Organoboron Polymers (<u>3c</u>-<u>3e</u>). **3c-3e** were obtained in quantitative yields by using similar procedure as described for **3b**. **3c** from **1** (0.109g, 1.11mmol) and **2c** (0.154g, 1.04mmol); ^{1}H-NMR (δ, ppm) 0.47-1.19 (-CH_3), 1.19-2.64 (-CH_2, -CH), 5.32-6.14 (C=C-H); IR (in $CHCl_3$) 2959, 2869, 1598, 1462, 1373, 1262, 1063cm^{-1}. **3d** from **1** (0.044g, 0.45mmol) and **2d** (0.072g, 0.41mmol); ^{1}H-NMR (δ, ppm) 0.45-1.07 (-CH_3), 1.07-2.52 (-CH_2, -CH), 5.28-5.74 (C=C-H); IR (in $CHCl_3$) 2960, 2870, 1603, 1462, 1372, 1062, 904cm^{-1}. **3e** from **1** (0.091g, 0.93mmol) and **2e** (0.119g, 0.88mmol); ^{1}H-NMR (δ, ppm) 0.57-1.06 (-C-CH_3), 1.08-2.54 (-CH_2, -CH, =C-CH_3), 5.30-5.87 (C=C-H); IR (in $CHCl_3$) 2957, 1606, 1463, 1374, 1238, 978, 909cm^{-1}.

References and Notes

1) Brown, H. C. *Hydroboration*, W. A. Benjamin, Inc.: New York, 1962.
2) Brown, H. C.; Zweifel, G. *J. Am. Chem. Soc.*, **1961**, <u>83</u>, 3834.
3) Dropping rate of **1** was fixed at 45μmol/min.
4) Detailed measurement conditions are described in Chapter 1.
5) Bubnov, Y. N.; Bogdanov, V. S.; Mikhailov, B. M. *Izv. Akad. Nauk SSSR, Ser. Khim.*, **1970**, 2416.
6) In ref. (1), p234.
7) See Section 1.
8) Odom, J. D. *Comprehensive Organomet. Chem.*, **1982**, <u>1</u>, 253.
9) Brown, H. C.; Mandal, A. K.; Kulkarni, S. U. *J. Org. Chem.*, **1977**, <u>42</u>, 1392.

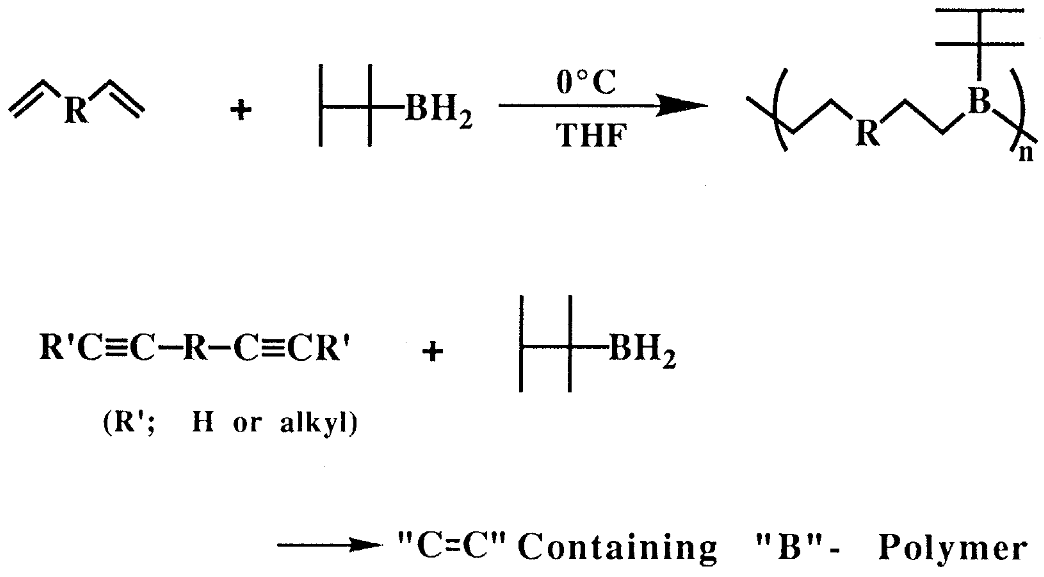
2 - 3

Synthesis of Organoboron Copolymers by the Reactions of Thexylborane with Dienes or Diene/Diyne.

Introduction

In the previous two sections, the author has described synthesis of organoboron polymers by the polyaddition of thexylborane with dienes, and with diynes, respectively (Scheme I). By using this polymerization method, organoboron polymers which can be regarded as a polymer homologue of trialkylboranes are produced. As trialkylboranes are very versatile reagents for the preparation of a wide variety of functional compounds in organic synthesis1), the organoboron polymers prepared by hydroboration polymerization can be expected as reactive polymeric materials to give other polymers having functional groups. Thus, it should be important to explore the possibilities of the preparative method for organoboron polymers. Here, copolymerizations by using two kinds of dienes, or diene/diyne systems were examined respectively by means of hydroboration polymerization.

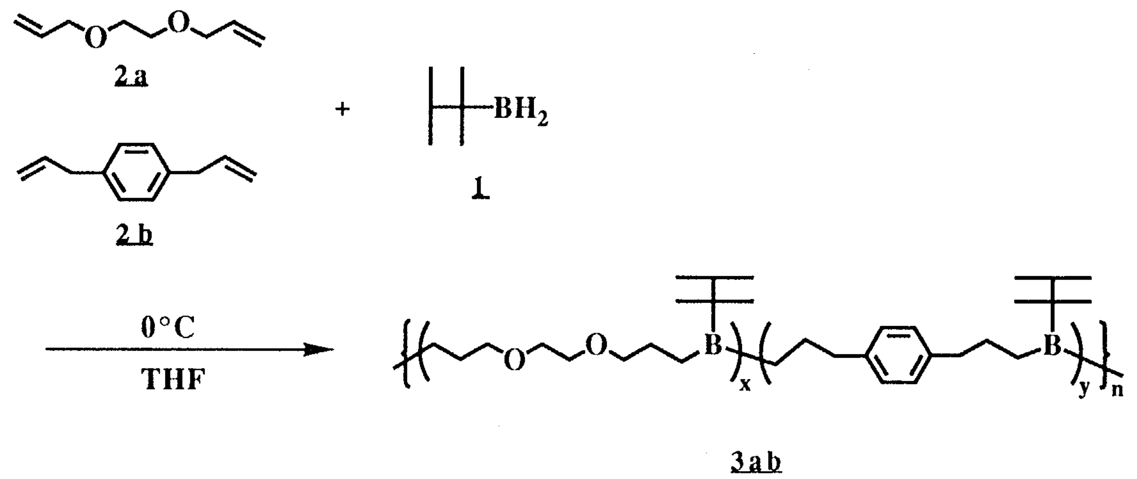
Scheme I



Results and Discussion

Copolymerization of Two Kinds of Dienes with 1. An organoboron polymer (**3a**) from 1,2-diallyloxyethane (**2a**) and **1** has no UV absorption, and the molecular weight of **3a** is rather low, possibly due to the disturbance of polymerization by the intramolecular coordination of oxygen atoms towards boron atoms in the main chain2). On the other hand, polymerization of *p*-diallylbenzene (**2b**) gives the corresponding high molecular weight polymer, which has strong UV absorption2). Thus, a set of these two dienes seems to be suitable for a study of copolymerization by means of GPC analyses using UV and RI detectors. First, polymerizations of a mixture of **2a**/**2b** (in 1:1 molar ratio) with various amounts of **1** were examined (Scheme II). The molecular weights of polymers obtained here (**3ab**) were estimated directly by GPC measurements (dried THF as an eluent, polystyrene standard) (Figure 1). In all cases, the peaks in GPC detected by UV had quite similar shapes to those detected by RI. The molecular weight of polymers (**3ab**) reached to its maximum when the feed ratio of **1** to (**2a**+**2b**) approached to unity, as was similar to the case of homopolymerization system using **1** and dienes2). ^{1}H-NMR and IR spectra of the polymer thus obtained were consistent with the expected copolymer.

Scheme II



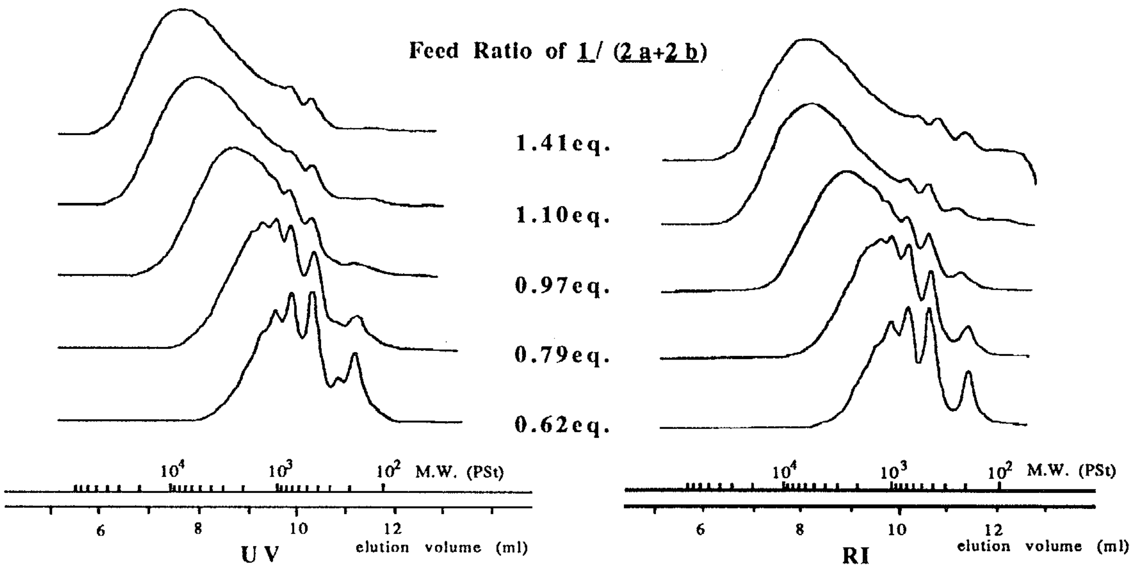


Figure 1 GPC traces of hydroboration copolymerization of 1 and 2a/2b.

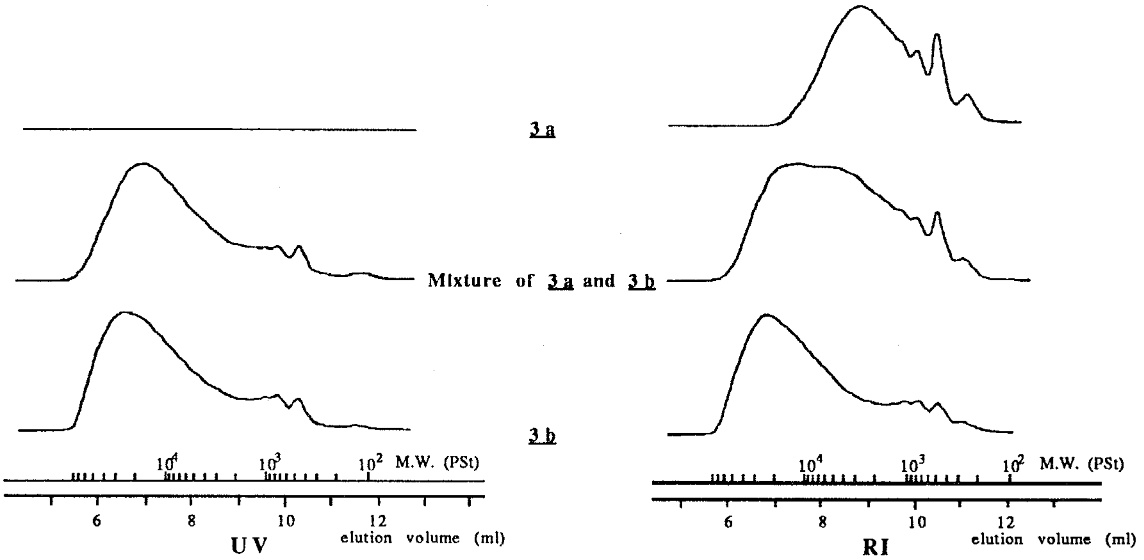


Figure 2 GPC traces of 3a, 3b, and a mixture of 3a and 3b.

The formation of copolymer by the present method was further confirmed by the comparison of GPC measurement with a mixture of two homopolymers between **3a** (prepared from **1** and **2a**) and **3b** (prepared from **1** and **2b**). As shown in Figure 2, the peaks of a mixture of homopolymers detected by UV were very similar to those of **3b**, whereas the corresponding peaks by RI were the sum of those of **3a** and **3b**. In other words, no specific interaction between **3a** and **3b** was observed in GPC measurement.

These results clearly show the formation of the corresponding copolymer. M_n and M_w of the obtained copolymer (**3ab**) were 2,340 and 6,400, respectively. This value was in between those of homopolymers **3a** (M_n=1,230 and M_w=2,980) and **3b** (M_n=12,600 and M_w=22,400) (Figure 3). In a similar manner, other copolymers were prepared from 1,7-octadiene (**2c**) and **2b**, or **2a** and *p*-divinylbenzene (**2d**) by the reaction with **1** (Table I).

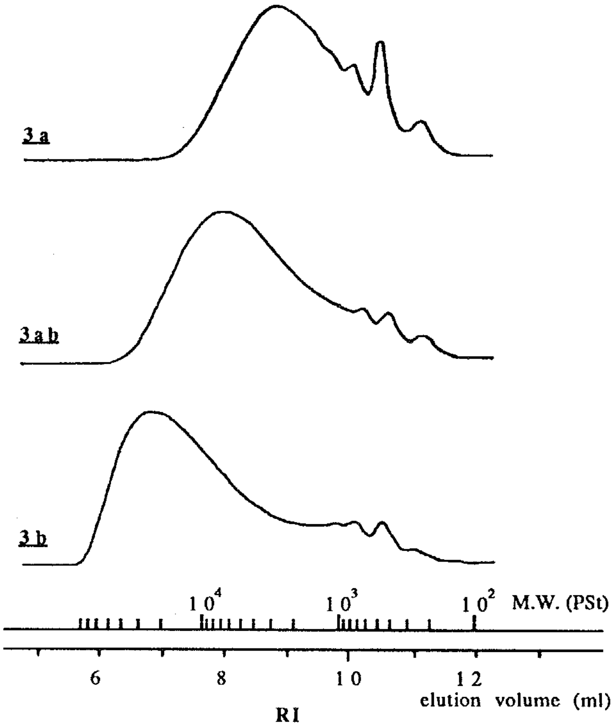
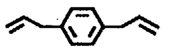
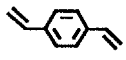
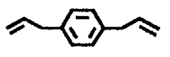
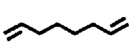
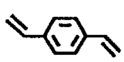


Figure 3 GPC traces of 3a, 3ab, and 3b.

Table I Synthesis of Organoboron Copolymers from Two Kinds of Dienes and Thexylborane.[a)]

Run	Dienes		$\overline{M}_n{}^{b)}$	$\overline{M}_w{}^{b)}$
1	 (2a)	 (2b)	2,340	6,400
2	 (2a)	 (2d)	2,900	9,720
3	 (2c)	 (2b)	10,700	15,900
4	 (2c)	 (2d)	13,000	24,100

a) Slightly excess of thexylborane (110-130%) was added to the THF solution of dienes by using microfeeder (45μmol/min.) at 0°C.

b) GPC (dried THF), polystyrene standard.

Copolymerization of Diene/Diyne System with 1. Hydroboration polymerization of terminal diynes gives organoboron polymers having branched structures due to the further hydroboration reaction towards the initially formed vinylborane structures[3]. That is, terminal diynes are taken to have a potential as a multifunctional monomers. Thus, hydroboration polymerization between 1,7-octadiene (**2c**) and **1** was examined in the presence of a small amount (0-5 mol% to **2c**) of 1,7-octadiyne (**4**) (Scheme III).

Scheme III

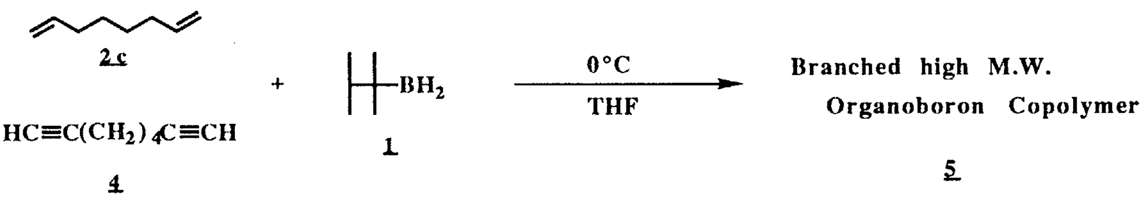


Table II Copolymerization of 1,7-Octadiene, 1,7-Octadiyne, and Thexylborane.[a]

Run	Diene (mmol)	Diyne (mmol)	Molar ratio	$\overline{M}_n$[b]	$\overline{M}_w$[b]
1[c]		-	-	20,100	36,600
2	1.39	0.027	50:1	16,700	63,200
3	1.41	0.071	20:1	27,600	214,000

a) Slightly excess of thexylborane (104-110%) was added to the THF solution of diene and diyne by using microfeeder (45μmol/min.) at 0°C.

b) GPC (dried THF), polystyrene standard.

c) Homopolymer prepared from thexylborane and 1,7-octadiene.

All the reactions were carried out by adding small excess amounts of **1** to a 2M THF solution of **2c**/**4** at 0°C. As shown in Table II, the molecular weight of the resulting polymer (**5**) was increased in the presence of **4** (run 1 vs. run 2). When 5 molar % of **4** was used, a gelation was observed. The gelation should be caused by the increase of crosslinking points in the polymer chains. The gel formed, however, was dissolved by the treatment with methanol[4]. As a result, GPC measurement was carried out after methanolysis (run 3). Although the number average molecular weights of copolymers (**5**) prepared by this method were comparable to that of homopolymer (**3c**), the weight average molecular weights were considerably increased. This copolymerization method using diyne may provide a synthetic route to obtain higher molecular weight (including gels) organoboron polymers.

Experimental Section

Materials and Instruments. Tetrahydrofuran was dried over lithium aluminum hydride and distilled before use. **2a** and **2c** were dried over sodium, and distilled before use. **2b**, **2d**, and **4** were distilled before use. ^{1}H-NMR spectra were recorded in $CDCl_3$ on a Hitachi R-600 instrument. IR spectra were obtained on a Perkin Elmer 1600 spectrometer. Gel permeation chromatographic analysis was carried out on a Tosoh HLC-8020 (TSK gel G3000, dried THF) after calibration with standard polystyrene samples.

Synthesis of Organoboron Copolymer (3ab) (Stoichiometric Studies). To a 1.6ml THF solution of **2a** (0.114g, 0.803mmol) and **2b** (0.128g, 0.808mmol), **1** (0.097g, 0.99mmol, 62% for dienes) was added by using a microfeeder (45μmol/min.) at 0°C under nitrogen atmosphere. This reaction mixture was kept stirring for an additional 1h, and was subjected directly to GPC measurement. To this reaction mixture, 0.027g, 0.029g, 0.021g, and then 0.049g (total 1.27mmol) of **1** were added stepwise using a microfeeder (45μmol/min.) at 0°C under nitrogen atmosphere. After the completion of each feeding, the reaction mixture was kept stirring for 1h, and was subjected directly to GPC measurement.

Synthesis of Organoboron Copolymers (3ad, 3bc, and 3cd). These organoboron copolymers were prepared in a similar manner to that for **3ab**. **3ad**: from **1a** (0.073g, 0.51mmol), **1d** (0.065g, 0.50mmol), and **1** (0.128g, 1.31mmol). **3bc**: from **1b** (0.102g, 0.64mmol), **1c** (0.072g, 0.66mmol), and **1** (0.146g, 1.49mmol). **3cd**: from **1c** (0.059g, 0.53mmol), **1d** (0.069g, 0.53mmol), and **1** (0.126g, 1.29mmol).

Synthesis of Organoboron Copolymer (5, in Table II, run 3). To a 0.7ml THF solution of **2a** (0.156g, 1.41mmol) and **2b** (0.0075g, 0.07mmol), **1** (0.159g, 1.62mmol) was added by using a microfeeder (45μmol/min.) at 0°C under nitrogen. When this reaction mixture was kept stirring for 30 min., gelation was observed. GPC was measured after dissolving this gel by the treatment with methanol (0.2ml). Similarly, a copolymer (**5**, in run 2) was prepared from **2a** (0.153g, 1.39mmol), **2b** (0.0029g, 0.03mmol), and **1** (0.156g, 1.59mmol). In this case, no gelation was observed even after 5h.

References and Notes

1) Pelter, A.; Smith, K.; Brown, H. C. *Borane Reagents*; Academic Press : London, 1988.
2) See Section 1.
3) See Section 2.
4) As discussed in Section 2, *gem*-diboramethylene should be cleaved easily under the protic condition.

Chapter 3

Reactions of Organoboron Polymers Prepared by Hydroboration Polymerization

ABSTRACT

Organoboron polymers prepared by "Hydroboration Polymerization" contain carbon-boron bonds in their main chains, which are regarded as a polymer homologue of trialkylborane. As to demonstrate the novel reactivity of these organoboron polymers, their several reactions to produce polymers having different backbones are examined in this chapter.

In 3-1, the reaction with carbon monoxide to produce the corresponding poly(alcohol)s is described. When an organoboron polymer prepared from 1,7-octadiene and thexylborane was reacted with carbon monoxide under rather forced conditions, a poly(alcohol) was obtained. When this reaction was carried out under milder conditions, a polymer having the structure of poly(alcohol)-co-poly(ketone) was formed. The conversions of organoboron polymers derived from various dienes were also examined to obtain the corresponding poly(alcohol)s.

Similarly, the reaction of an organoboron polymer with potassium cyanide followed by the oxidative treatment to produce a poly(ketone) is described in 3-2. In this reaction system, the obtained polymer was found to contain only ketone segments in its main chain.

3-3 describes the reaction of organoboron polymers with α,α-dichloromethyl methyl ether (DCME) in place of carbon monoxide, followed by the oxidative treatment to obtain the poly(alcohol)s in high yields. In this reaction system, poly(alcohol)s having the identical structures to those obtained in Chapter 4 could be prepared under milder conditions.

In 3-4, synthesis of poly(alcohol)s having primary and tertiary hydroxyl groups by the reaction of organoboron polymers with α-furyllithium is described. This reaction might include an intramolecular rearrangement of polymer chains of organoboron polymer and a ring-opening of furan rings.

In 3-5, polymers having cyano groups were obtained by the reaction of organoboron polymers with 2-bromo-6-lithiopyridine. This reaction also accompanies a ring-opening reaction of pyridine moieties during the migration reaction. The polymers obtained

here indicated almost the same molecular weights as those of starting organoboron polymers.

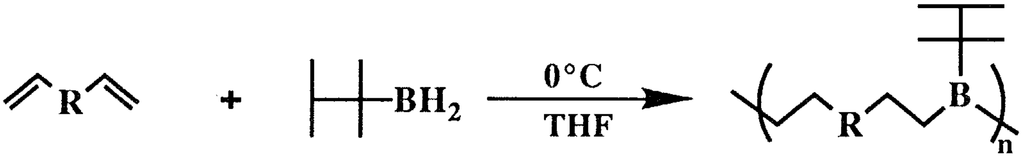
3 - 1

Synthesis of Poly(alcohol)s by the Reaction with Carbon Monoxide.

Introduction

A wide variety of reactions of organoboron compounds have been investigated in organic synthesis1) together with the progress of the chemistry of hydroboration. In the field of polymer synthesis, however, applications of these reactions have been achieved only in the oxidation of poly(olefin)s to poly(alcohol)s2). In Chapter 2, the author has described "Hydroboration Polymerization", in which organoboron polymers were produced by a polyaddition between diene and thexylborane (Scheme I).

Scheme I



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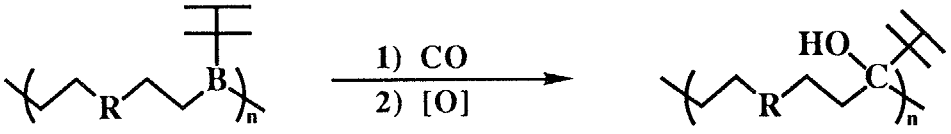
As the organoboron polymers obtained by hydroboration polymerization are regarded as a polymer homologue of trialkylborane, these new polymeric materials should have possible potentials as a novel reactive polymer.

In general, poly(alcohol)s have interesting characteristics that can be applied as coatings, adhesives, and polymeric reagents3). However, the general synthetic methods for the preparation of poly(alcohol)s have been limited so far. The present section describes a novel synthetic method for the preparation of poly(alcohol) by the reaction of organoboron polymers with carbon monoxide followed by an oxidative treatment.

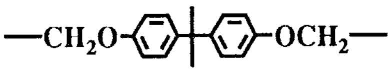
Results and Discussion

Organoboron compounds are known to react with carbon monoxide to produce alcohols, aldehydes, or ketones4). The products can be varied by changing the additional reagents and reaction conditions. To convert boron-alkyls into alcohols and ketones, their reactions with α,α-dichloromethyl methyl ether5) and with cyanide anion6) are also available, respectively. In order to investigate a series of reactions of organoboron polymers, the reaction with carbon monoxide was examined here (Scheme II).

Scheme II



1 2

	R
a	$—(CH_2)_4—$
b	$—(CH_2)_6—$
c	
d	
e	$—CH_2OCH_2CH_2OCH_2—$
f	$—CH_2O(CH_2)_4OCH_2—$
g	$—CH_2O(CH_2CH_2O)_3CH_2—$
h	
i	

The starting organoboron polymers (**1a**-**1i**) were obtained easily by the reaction of the corresponding dienes and thexylborane under mild conditions7). When 1,7-octadiene was used as the diene monomer, M_n and M_w of the obtained polymer (**1a**) were 19,500 and 27,700, respectively (GPC, dry THF, polystyrene standard). In order to optimize the conditions of the reaction with carbon monoxide, this polymer (**1a**) was subjected to the reaction. The polymer obtained by hydroboration polymerization was used without further purification and was reacted directly with carbon monoxide in an autoclave. Details of the reaction conditions are described in the experimental section. The results are summarized in Table I.

Under the forced reaction conditions, e.g., at 120°C, the obtained polymer (**2a**) after oxidation was found to consist exclusively of alcohol segment (run 1). On the contrary, under the milder conditions, e.g., at 50°C, the obtained polymer was found to consist both of alcohol and ketone segments (run 2) from their ^{1}H-NMR and IR analyses. Typical examples of ^{1}H-NMR and IR spectra of poly(alcohol) and poly(alcohol)-co-poly(ketone) are shown in Figure 1 and Figure 2, respectively.

Table I Reactions of Organoboron Polymer (1a) with Carbon Monoxide.

Run	Conditions	Composition[f]		$\overline{M}_n$[g]	Yield[h] (%)
		alcohol	ketone		
1	50°C 15h, 120°C 5h[a]	100	0	4,080	82
2	50°C 15h[b]	50	50	2,500	80
3	r.t. 18h[b]	32	68	2,500	61
4	0°C 15h[b]	34	66	590	67
5	-25°C 40h[c]	-	-	-	0
6	50°C 15h[d]	35	65	3,900	n.d.[i]
7	50°C 15h[e]	-	-	gelation	-

a) Run 1: 50°C 15h (CO;25kg/cm^2), and then 120°C 5h (after CO was released).

b) Runs 2-4: CO; 20-25kg/cm^2. c) Run 5: CO; 30-35kg/cm^2.

d) H_2O (1 eq.) was added at the carbonylation stage (CO; 30-35kg/cm^2).

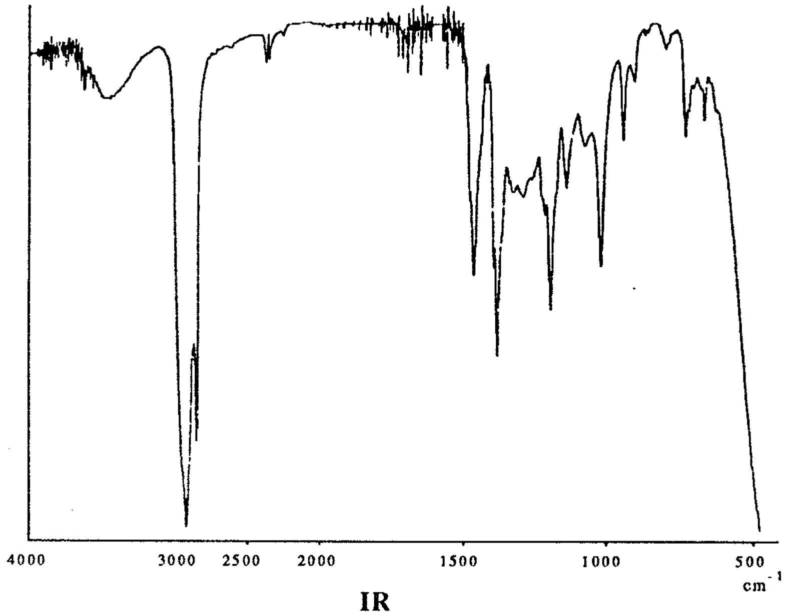
e) In the absence of ethylene glycol.

f) Calculated from ^{1}H-NMR. g) GPC (THF), Polystyrene standard.

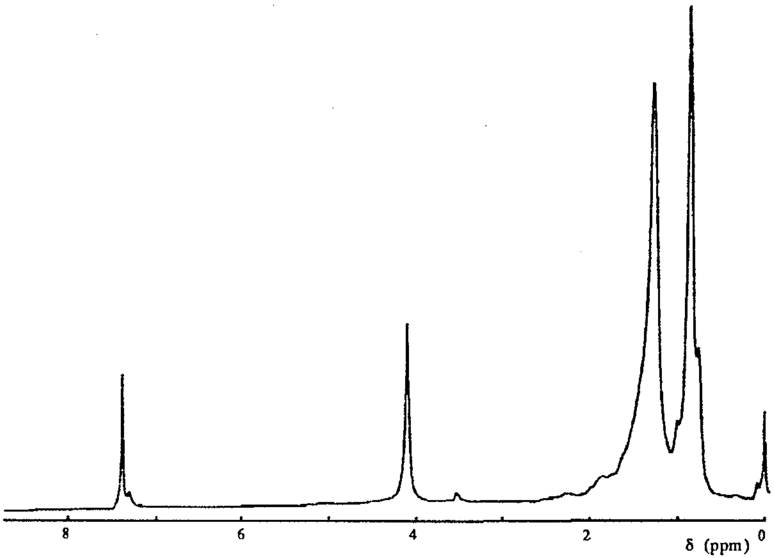
h) Isolated yields after reprecipitation into methanol/water (v/v=2/1).

i) Not determined.

As shown in Figure 1, no peak due to the stretching of C=O was observed around 1700cm^{-1} in its IR, and the integral area ratio between thexyl protons and methylene protons in its ^{1}H-NMR was in good agreement with the calculated value. In Figure 2, however, the stretching band of C=O at 1702cm^{-1} was observed in its IR, and new peaks at 2.38ppm assignable to the methylene protons adjacent to C=O were observed accompanied by a decrease of protons of thexyl groups in its ^{1}H-NMR. The compositions of alcohol segments and ketone segments can be estimated from the integral ratio between thexyl protons and methylenes. These values are also summarized in Table I. According to the proposed mechanism for the reaction of organoboron compounds with carbon monoxide[4c)], the present polymer reaction can be considered to proceed as shown in Scheme III.

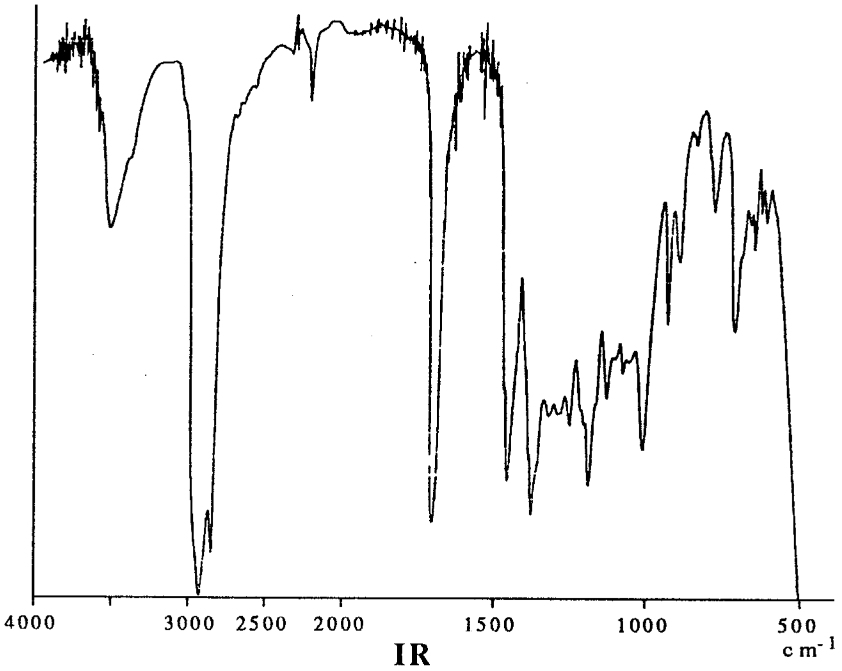


IR



^{1}H-NMR

Figure 1 IR and ^{1}H-NMR spectra of poly(alcohol) (2a, Table I, run 1).



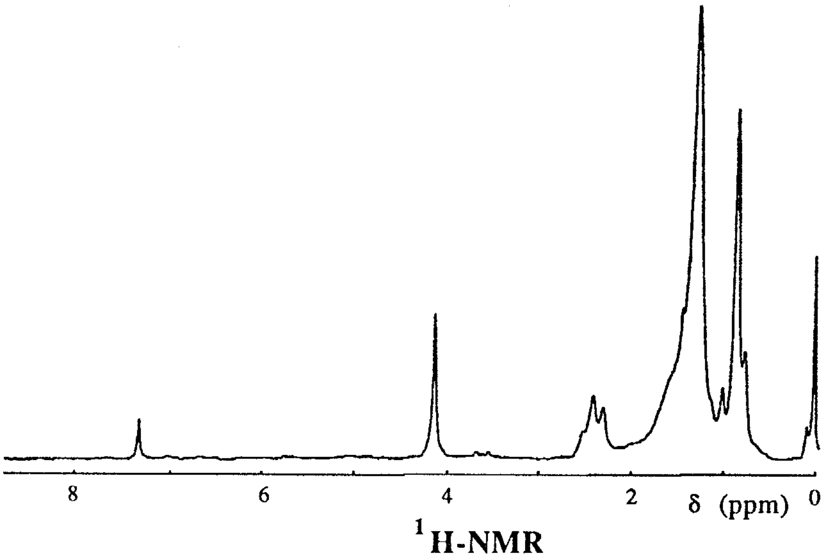
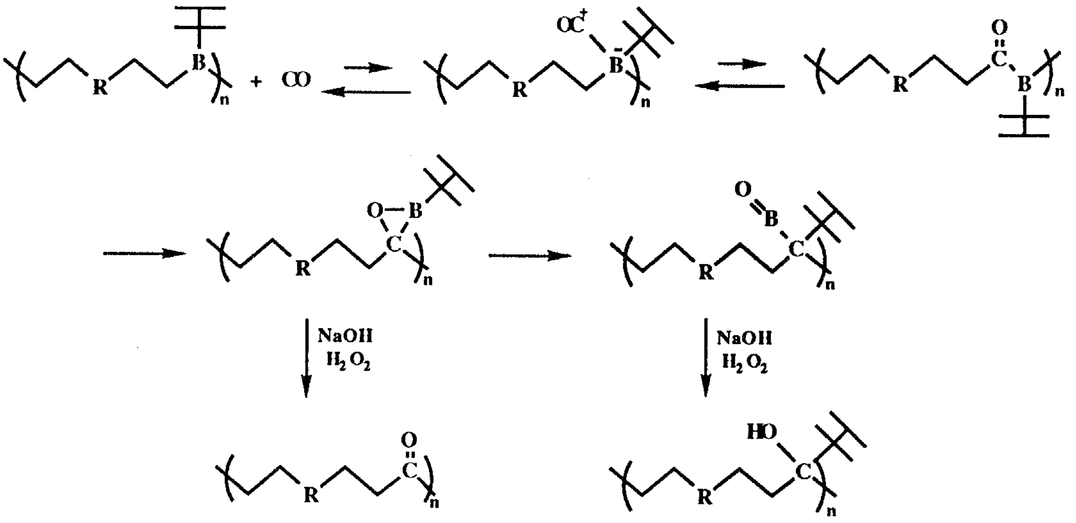


Figure 2 IR and ^{1}H-NMR spectra of poly(alcohol)-co-poly(ketone) (2a, Table I, run 2).

A primary alkyl group is known to be more reactive than a tertiary alkyl group in this intramolecular rearrangement reaction[4d]. Thus, it is reasonable to suppose that the migration of main chain methylene groups of organoboron polymer (mostly consisting of primary alkyl group) is more likely to occur than that of thexyl group.

Scheme III

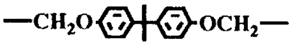


This different reactivity made it possible to include ketone segments without obvious scission of the polymer chain, though the molecular weight of the obtained polymer was decreased due to the unreacted unit of boron-methylene linkage, as the reaction condition became milder. Under much milder condition, e.g., at -25°C (run 5), this migration reaction did not occur and resulted only in the decomposition of the starting polymer.

The obtained poly(alcohol) was a white gum, and was soluble in organic solvents such as THF and chloroform. These polymers were obviously air stable. This migration reaction is known to proceed intramolecularly. Thus, it can be mentioned that the molecular weight of the starting organoboron polymers should be higher than (or the same as) that of poly(alcohol)s.

Poly(alcohol)s from Various Organoboron Polymers. As mentioned above, selective conversion of organoboron polymer to the corresponding poly(alcohol) was possible under the forced reaction condition. When other organoboron polymers (**1b**-**1i**) were subjected to this reaction at 120°C, the corresponding poly(alcohol)s were obtained. The results are summarized in Table II. These conversions may offer a new synthetic method for poly(alcohol)s from the corresponding dienes.

Table II Synthesis of Poly(alcohol)s (2a-2i) from Various Organoboron Polymers (1a-1i)[a].

			B-Polymers (1)	Poly(alcohol)s (2)		
Run	R		M_n[b]	M_n[c]	M_w[c]	Yield[d] (%)
1	$-(CH_2)_4-$	(a)	19,500	4,080	13,500	82
2	$-(CH_2)_6-$	(b)	20,500	4,200	9,600	60
3		(c)	14,600	2,990	7,650	74
4		(d)	9,300	5,400	12,300	77
5	$-CH_2O(CH_2)_2OCH_2-$	(e)	1,520	1,280	2,200	24
6	$-CH_2O(CH_2)_4OCH_2-$	(f)	2,280	1,620	2,800	59
7	$-CH_2O\{(CH_2)_2O\}_3CH_2-$	(g)	3,200	2,200	3,720	47
8		(h)	6,800	1,940	3,700	39
9		(i)	11,700	2,320	4,400	89

a) Reactions were carried out in the presence of 0.1ml ethylene glycol under carbon monoxide (20-25 kg/cm^2) in an autoclave.

b) GPC (dry THF, PSt, Std). c) GPC (THF, PSt, Std).

d) Isolated yield after reprecipitation into methanol/water (v/v=2/1).

Experimental Section

Materials and Instruments. Tetrahydrofuran was dried over lithium aluminum hydride and distilled before use. Ethylene glycol was dried over sodium and distilled under reduced pressure. Sodium hydroxide, hydrogen peroxide (30%), benzene, and methanol were used without purification.

^1H-NMR spectra were recorded in $CDCl_3$ on a Hitachi R-600 instrument. IR spectra were obtained on a Perkin Elmer 1600 spectrometer. Gel permeation chromatographic analyses were carried out on a Tosoh HLC-8020 (TSK gel G3000) after calibration with standard polystyrene samples.

Synthesis of Poly(alcohol)s from Organoboron Polymers: A typical procedure (Table I, Run 1). The organoboron polymer (**1a**) was prepared as shown in Chapter 1, and was used without isolation. To a nitrogen purged autoclave (30ml) equipped with a magnetic stirrer tip, were added a THF solution (5ml) of **1a** (prepared from 0.189g, 1.72mmol of 1,7-

octadiene and 0.172g, 1.75mmol of thexylborane) and ethylene glycol (0.2ml). Carbon monoxide was charged (20-25kg/cm^2) from a cylinder. After heating at 50°C for 15h, carbon monoxide was purged out and the temperature was raised to 120°C for additional 5h. The reaction mixture was treated with aqueous sodium hydroxide (6N, 4ml) and hydrogen peroxide (30%, 4ml) at 50°C for 3h. This mixture was extracted with diethyl ether, dried over sodium sulfate, and concentrated. To remove contaminated boronic acid, the obtained polymer was subjected to ten times evaporation with methanol/benzene under normal pressure$^{8)}$. After precipitation into MeOH/H_2O (v/v= 2/1), **2a** was obtained as a colorless gum (0.319g, 82% yield). ^{1}H-NMR and IR data are given in Figure 1. Poly(alcohol)-poly(ketone) from **1a** (in Table I, Runs 2-7) was prepared in a similar manner except the reaction conditions as follows; Table I, Run 2; 15h at 50°C with 20-25kg/cm^2 of carbon monoxide, Run 3; 15h at ambient temperature with 20-25kg/cm^2 of carbon monoxide, Run 4; 18h at 0°C with 20-25kg/cm^2 of carbon monoxide, Run 5; 40h at -25°C with 30-35kg/cm^2 of carbon monoxide, Run 6; 15h at 50°C with 30-35kg/cm^2 of carbon monoxide in the presence of an equivalent molar of water, Run 7; 15h at 50°C with 30-35kg/cm^2 of carbon monoxide without ethylene glycol.

Various poly(alcohol)s were prepared in the same manner as described above. **2b**: ^{1}H-NMR (δ, ppm) 0.55-1.06 (-CH_3, 12H), 1.06-2.01 (-CH, -CH_2, 21H); IR (neat) 3447, 2852, 1465, 1383, 1196, 1022cm^{-1}. **2c**: ^{1}H-NMR (δ, ppm) 0.59-1.15 (-CH_3, 12H), 1.15-2.31(-CH, -CH_2, 5H), 2.36-3.13 (Ph-CH_2, 4H), 7.20 (C_6H_4, s, 4H); IR (neat) 3482, 2961, 1513, 1465, 1382, 1042, 909, 734cm^{-1}. **2d**: ^{1}H-NMR (δ, ppm) 0.55-1.15 (-CH_3, 12H), 1.25-2.85 (-CH, -CH_2, 13H), 7.07 (C_6H_4, 4H); IR (cell, $CHCl_3$) 3616, 2960, 1463, 1384, 1020, 906cm^{-1}. **2e**: ^{1}H-NMR (δ, ppm) 0.63-1.19 (-CH_3, 12H), 1.33-2.17 (-CH, -CH_2, 9H), 3.17-3.91 (-OCH_2, 8H); IR (neat) 3474, 2959, 1465, 1381, 1120cm^{-1}. **2f**: ^{1}H-NMR (δ, ppm) 0.55-1.15 (-CH_3, 12H), 1.33-2.37(-CH, -CH_2, 13H), 3.15-3.97 (-OCH_2, 8H); IR (neat) 3446, 2945, 1471, 1367, 1111cm^{-1}. **2g**: ^{1}H-NMR (δ, ppm) 0.59-1.13 (-CH_3, 12H), 1.31-2.35(-CH, -CH_2, 9H), 3.09-3.91 (-OCH_2, 16H); IR (neat) 3465, 2868, 1464, 1382, 1115cm^{-1}. **2h**: ^{1}H-NMR (δ, ppm) 0.63-1.13 (-

CH_3, 12H), 1.13-2.35 (-CH, -CH_2, 9H), 3.66-4.27 (-OCH_2, 4H), 6.83 (C_6H_4, s, 4H); IR (neat) 3508, 2957, 1506, 1471, 1382, 1228, 1030, 824cm^{-1}. **2i**: ^{1}H-NMR (δ, ppm) 0.57-1.11 (-CH_3, 12H), 1.33-2.38(-CH, -CH_2, -CH_3, 15H), 3.58-4.36 (-OCH_2, 4H), 6.57-7.30 (C_6H_4, 8H); IR (neat) 3510, 2965, 1608, 1510, 1472, 1248, 1181, 1011, 910, 829, 735cm^{-1}.

References and Notes

1) (a) Pelter, A.; Smith, K.; Brown, H. C. *Borane Reagents*; Academic Press: London, 1988. (b) Brown, H. C. *Organic Synthesis via Boranes*; Wiley-Interscience: New York, 1975.
2) (a) Chung, T. C. *Macromolecules*, **1988**, 21, 865. (b) Chung, T. C. *J. Polym. Sci.: Part A: Polym. Chem.*, **1989**, 27, 3251. (c) Ramakrishnan, S.; Berluche, E; Chung, T. C. *Macromolecules*, **1990**, 23, 378.
3) Akelah, A.; Sherrington, D. C. *Chem. Rev.*, **1981**, 557.
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5) In ref. (1a), p272.
6) In ref. (1a), p280.
7) See Chapter 2, Section 1.
8) If this procedure was omitted, the obtained poly(alcohol) became insoluble due to the crosslinking reaction of alcohol moieties with boronic acid.

3 - 2

Selective Synthesis of Poly(ketone) by the Reaction with Cyanide Anion.

Introduction

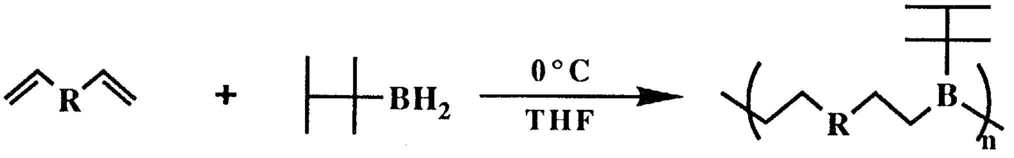
Reactions of organoboron compounds with cyanide anion in the presence of acylating reagents such as trifluoroacetic anhydride (TFAA) are reported to produce the corresponding ketons1). Numerous numbers of reports have dealt with this reaction2). Organoboron polymers prepared by "Hydroboration Polymerization" are regarded as a polymer homologue of trialkylborane, and they can be considered to be a novel type of reactive polymers. In 3-1, the reaction of organoboron polymers with carbon monoxide to produce the corresponding poly(alcohol)s has been described. In this section, the direct use of the migration reaction of organoboron polymers with cyanide anion to produce a polymeric ketone was examined.

Results and Discussion

The starting organoboron polymer (**1**) was obtained easily by the reaction of 1,7-octadiene and thexylborane under mild conditions (Scheme I)3). As a preliminary experiment, **1** was subjected to the reaction with potassium cyanide (Scheme II). Details of the reaction conditions are described in the experimental section.

After the oxidation of the reaction mixture followed by the coagulation with methanol, the desired poly(ketone) (**2**) was obtained in a yield of 39%. The obtained poly(ketone) (**2**) was a white solid, and was soluble in chloroform. **2** was stable enough under air. This stability indicates no C-B bonds in the main chain of the resulting polymer. The number average molecular weight of **2** was estimated to be 1,300 from GPC ($CHCl_3$ as an eluent) by using polystyrene calibration curves. This value is somewhat lower than that of poly(alcohol)s obtained by the reaction of the organoboron polymer with carbon monoxide4).

Scheme I



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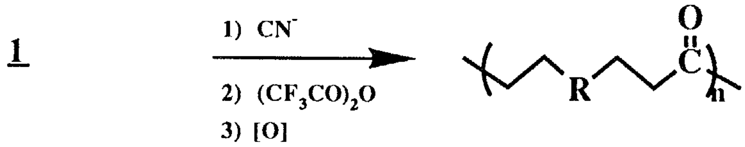
Scheme II



2

According to the proposed mechanism for the reaction of organoboron compounds with cyanide anion1), the present polymer reaction can be described to proceed as shown in Scheme III. Primary alkyl group is known to be more reactive than tertiary alkyl group in this intramolecular rearrangement1). Thus, it is possible to make a poly(ketone) by the exclusive migration of main chains of the organoboron polymer (consisting of primary alkyl groups). Although the difference of reactivity between methylene group and thexyl group seems to be large enough, the molecular weight of the obtained poly(ketone) was lower than expected. The reaction for thexyldialkylborane has been reported to be not quantitative (76-85%)1). The present reaction proceeds stepwise, i.e., the formation of poly(anion) followed by the migration. Accordingly, before adding TFAA, it is necessary to form a poly(anion) completely. This step may require the severe condition due to the repulsion of the charge in the poly(anion). The remained neutral boron should result in the scission of the expected polymer after the oxidation of C-B bonds. This point is entirely different from the reaction with carbon monoxide in which the migration reaction does not proceed stepwise. These may be the reasons of low molecular weight of poly(ketone) obtained.

Table I summarizes the results of preparation of poly(ketone) under various conditions.

Scheme III

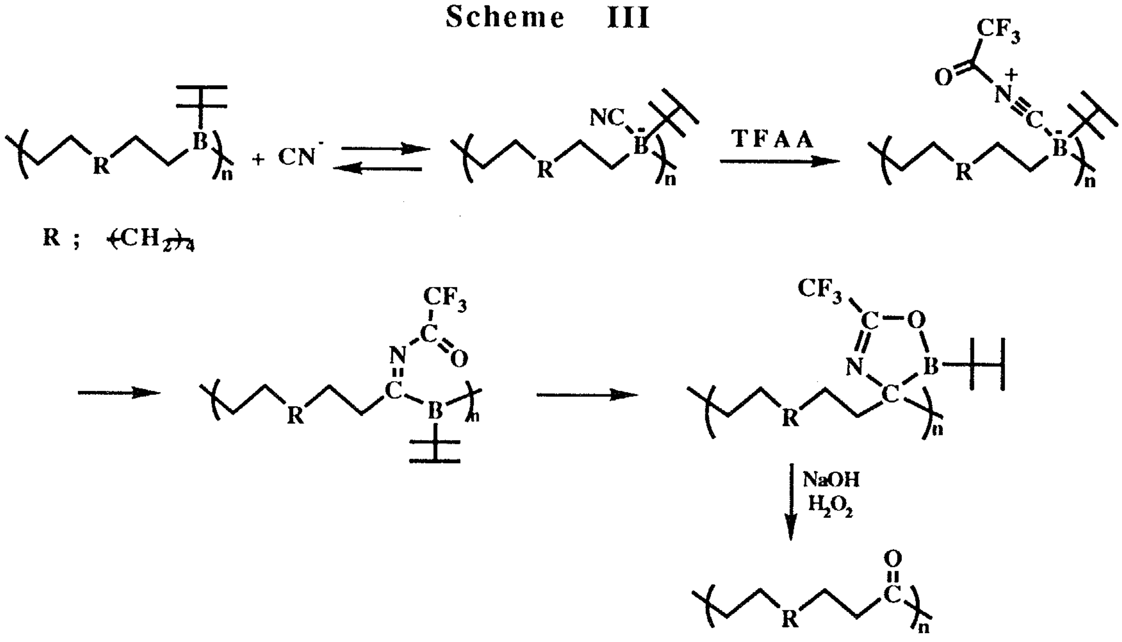
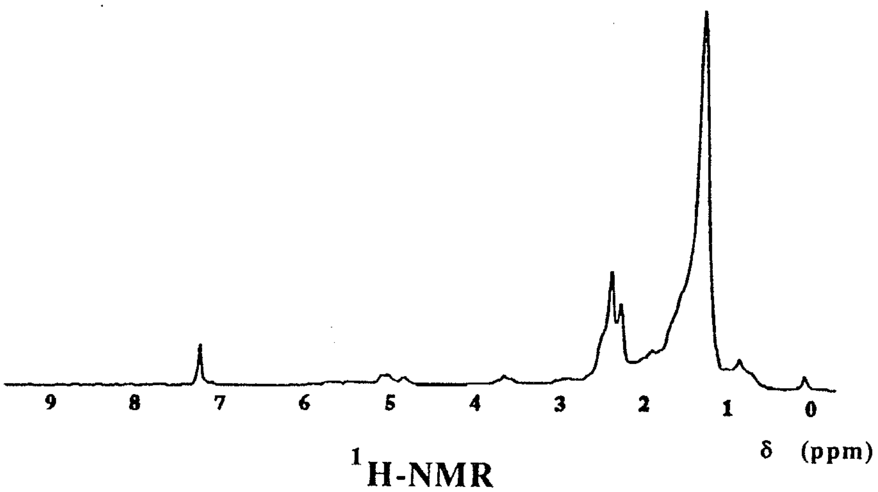


Table I Synthesis of Poly(ketone) by the Reaction of **1** with KCN and TFAA[a].

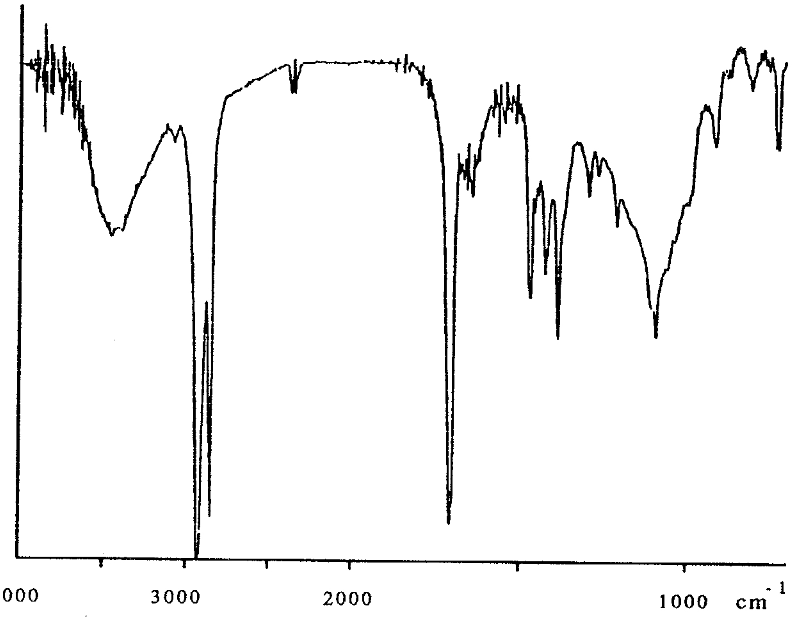
Run	Reaction Conditions		Yield(%)[b]	$\overline{M}_n$[c]
	KCN	TFAA		
1	60°C 1.5h	50°C 4h	29	1,800
2	40°C 1h	50°C 3h	39	1,300
3	rt 1h	50°C 1h	10	-
4	rt	rt	6	-

a) Reactions were carried out in THF.
b) Isolated yields after reprecipitation into methanol.
c) GPC ($CHCl_3$, polystyrene standard).

^{1}H-NMR and IR spectra of **2** are represented in Figure 1. In its IR spectrum, a strong peak due to the stretching of C=O was observed around 1710cm^{-1}. In its ^{1}H-NMR, the integral ratio between the protons of inner methylenes and methylene protons adjacent to carbonyl group was in good agreement to the calculated value.



^{1}H-NMR



IR

Figure 1 ^{1}H-NMR and IR spectra of poly(ketone) (2).

The fact that this migration reaction proceeds intramolecularly$^{1)}$ also supports the formation of polymeric organoboron species by hydroboration polymerization. Although the molecular weight of the obtained polymer is not enough high at the present time, the present conversion reaction of organoboron polymers provides a new synthetic method to prepare poly(ketone)s.

Experimental Section

Materials and Instruments. Tetrahydrofuran was dried over lithium aluminum hydride and distilled before use. TFAA was purified as usual technique. Potassium cyanide, sodium hydroxide, hydrogen peroxide (30%), and methanol were used without further purification.

^{1}H-NMR spectrum was recorded in $CDCl_3$ on a Hitachi R-600 instrument. IR spectrum was obtained on a Perkin Elmer 1600 spectrometer. Gel permeation chromatographic analyses were carried out on a Jasco Triroter (Shodex AC803, $CHCl_3$) after calibration with standard polystyrene samples.

Synthesis of Poly(ketone) (2) from Organoboron Polymer (1). The organoboron polymer (1) was prepared according to the procedure shown in 2-1, and was used without isolation. To well dried potassium cyanide (0.36g, 5.5mmol) was added a 5ml THF solution of **1** (prepared from 0.55g, 5.0mmol of 1,7-octadiene and 0.49g, 5.0mmol of thexylborane) under nitrogen. This reaction mixture was stirred for 1h at 40°C. TFAA (1.26g, 6mmol) was added and the mixture was allowed to keep for 3h at 50°C. The reaction mixture was treated with aqueous sodium hydroxide (6N, 3ml) and hydrogen peroxide (30%, 8ml) at 50°C for 4h. The organic layer was dried over sodium sulfate, and concentrated. After precipitation into methanol, **2** was obtained as a white solid (0.27g, 39% yield). ^{1}H-NMR and IR spectra are shown in Figure 1.

References

1) (a) Pelter, A.; Smith, K.; Hutchings, M. G.; Rowe, K. *J. Chem. Soc. Perkin I,* **1975**, 129. (b) Pelter, A.; Hutchings, M. G.; Rowe, K.; Smith, K. *ibid.,* **1975**, 138.
2) Pelter, A.; Smith, K.; Brown, H. C. In *Borane Reagents*; Academic Press: London, 1988 p280 and references cited therein.
3) See Chapter 2, Section 1.
4) See 3-1.

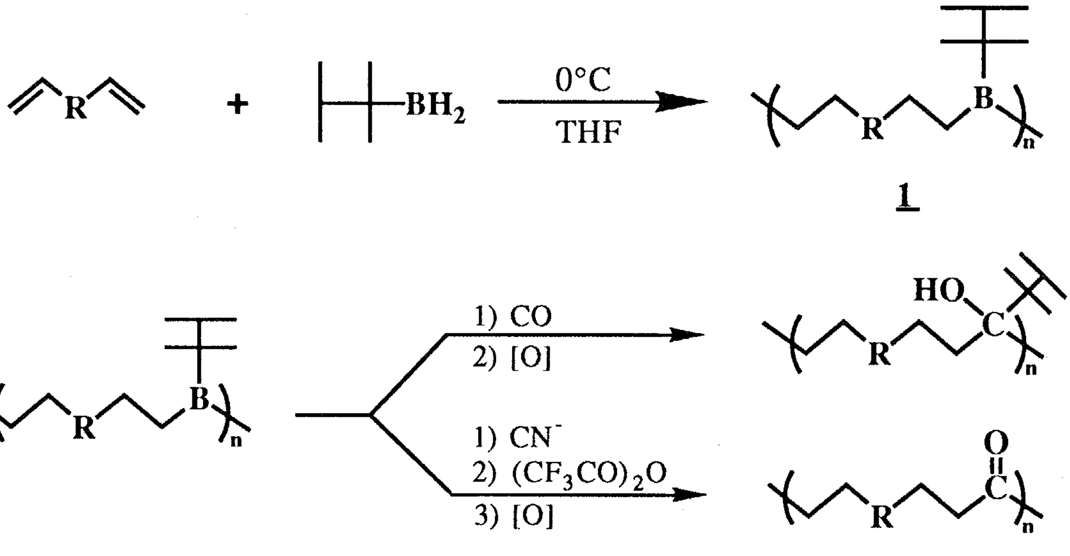
3 - 3

Synthesis of Poly(alcohol)s by the Reaction with α,α-Dichloromethyl Methyl Ether.

Introduction

In 3-1 and 3-2, versatile reactions of organoboron polymers to produce poly(alcohol)s and poly(ketone) are described (Scheme I). Synthesis of polymers having these structures are quite difficult by the conventional known methods. The novel polymer reaction to obtain poly(alcohol)s from carbon monoxide and organoboron polymers may give a useful synthetic way, in which the length of methylene chains between the alcohol moieties can be strictly controlled by changing the diolefins used for the synthesis of starting organoboron polymers.

Scheme I

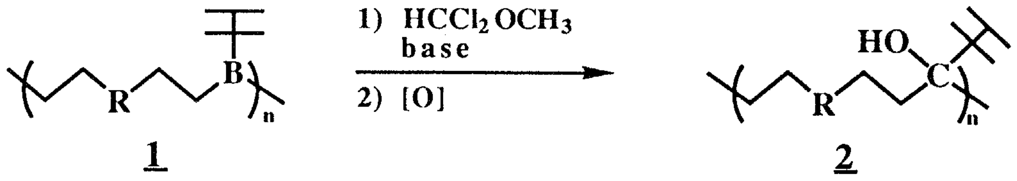


In the migration reaction of trialkylborane, α,α-dichloromethyl methyl ether (DCME) is known to serve as an equivalent of carbon monoxide. Therefore, an alternative method to convert organoboron polymers into poly(alcohol)s by using DCME is described here.

Results and Discussion

Tertiary alcohols are obtained from trialkylboranes by the reaction with α,α-dichloromethyl methyl ether (DCME)1) as well as by the reaction with carbon monoxide2). The present migration reaction using DCME is known to proceed intramolecularly. Due to the high conversion of this reaction, the formation of poly(alcohol)s by the reaction of organoboron polymers with DCME can be expected (Scheme II).

Scheme II



Organoboron polymers (**1a**-**1i**) were prepared by hydroboration polymerization starting from various diolefins and thexylborane as described in 2-1, and were used without isolation. As a typical example, an organoboron polymer (**1a**) was prepared from thexylborane and 1,7-octadiene. The number-average molecular weight of the obtained polymer (**1a**) was 12,700, which was determined by GPC on the basis of polystyrene standard samples.

Conversions of the organoboron polymers (**1a**-**1i**) into poly(alcohol)s (**2a**-**2i**) were examined by adding 1.2eq. of DCME to a THF solution of **1a**-**1i** followed by the treatment with 1.5eq. of Et_3COLi in *n*-hexane. After the oxidative treatment with $NaOH/H_2O_2$, the corresponding poly(alcohol)s were obtained. The obtained poly(alcohol)s, however, became insoluble when the solvents were completely removed, due to the crosslinking reaction with contaminated boronic acid. Thus, after careful treatment with hot methanol, these poly(alcohol)s could be successfully isolated as THF-soluble materials in almost quantitative yields based on the starting dienes.

Table I summarizes the results of reactions of various organoboron polymers with DCME to produce the corresponding poly(alcohol)s. The molecular weights of the starting organoboron polymers are also shown in this table. According to the reaction mechanism for trialkylboranes1), the present reaction can be taken to proceed as shown in Scheme III. That is, carbanion having three leaving groups (generated *in situ* by means of hindered base) attacks boron atom, and then triple migration takes place intramolecularly. In the case of incomplete migration, the boron atom is remained in the main chain, which causes a scission of the polymer. M_n of poly(alcohol) (**2a**) obtained from **1a** was estimated to be 3,600 (GPC, based on polystyrene calibration curves). Although the direct comparison of the molecular weights between the starting organoboron polymers and the obtained poly(alcohol)s has little meanings (both of these are calculated from the standard polystyrene samples), only small amounts of scission at C-B bond in the main chain of the starting polymers (1 or 2 points per polymer chain) might take place under the examined reaction conditions.

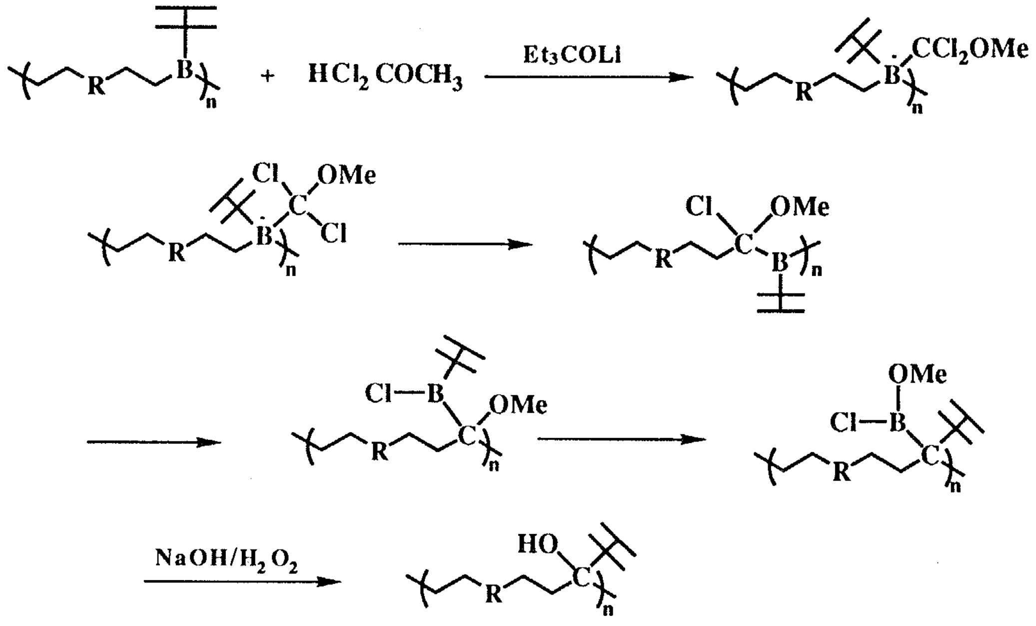
Table I Synthesis of Poly(alcohol)s (2a-2i) from Various Organoboron Polymers (1a-1i)a).

Run	R		B-Polymers (1)	Poly(alcohol)s (2)	
			$\overline{M}_n$ b)	$\overline{M}_n$ c)	$\overline{M}_w$ c)
1	$-(CH_2)_4-$	(a)	12,700	3,600	10,600
2	$-(CH_2)_6-$	(b)	18,400	4,900	14,700
3		(c)	19,200	2,200	5,400
4		(d)	9,400	1,700	9,700
5	$-CH_2O(CH_2)_2OCH_2-$	(e)	1,200	780	1,600
6	$-CH_2O(CH_2)_4OCH_2-$	(f)	1,900	560	1,200
7	$-CH_2O\{(CH_2)_2O\}_3CH_2-$	(g)	1,900	550	1,300
8		(h)	5,100	1,300	2,400
9		(i)	7,600	2,300	4,700

a) After adding 1.2eq. of DCME to a THF solution of organoboron polymers, 1.5eq. of Et_3COLi/*n*-hexane was added at 0°C.
b) GPC (dry THF, PSt, Std). c) GPC (THF, PSt, Std).

The reaction with DCME as well as that with carbon monoxide may offer a useful synthetic way to obtain poly(alcohol)s. Because the reaction with carbon monoxide requires relatively severe conditions (120°C, 30kg/cm^2), the reaction with DCME provides more facile way for the conversion of organoboron polymers into poly(alcohol)s under mild conditions.

Scheme III



Experimental Section

Materials and Instruments. Tetrahydrofuran was dried over lithium aluminum hydride and was distilled before use. Commercially available DCME was distilled before use. Sodium hydroxide, hydrogen peroxide (30%), benzene, and methanol were used without further purification.

^{1}H-NMR spectra were recorded in $CDCl_3$ on a Hitachi R-600 instrument (60MHz). IR spectra were obtained on a Perkin Elmer 1600 spectrometer. Gel permeation chromatographic analyses were carried out on a Tosoh HLC-8020 (TSK gel G3000) after calibration with standard polystyrene samples.

Synthesis of poly(alcohol) (2a) from Organoboron Polymer (1a). A typical procedure is shown as follows. To a THF solution of **1a** prepared from 1,7-octadiene (0.189g, 1.72mmol) and thexylborane (0.173g, 1.76mmol), was added DCME (0.228g, 1.98mmol) and Et_3COLi in *n*-hexane (1.36N, 2.2ml) at 0°C under nitrogen. The reaction mixture was stirred for 1 day at room temperature. After the treatment with aqueous sodium hydroxide (6N, 6ml) and hydrogen peroxide (30%, 6ml) at 50°C for 3h, the reaction mixture was extracted with three 50ml portions of THF and dried over sodium sulfate. After evaporation with methanol/benzene (ten times) under normal pressure, freeze-drying with benzene gave **2a** in a quantitative yield. When this crude product was reprecipitated into ethanol/water (v/v=1/1), 0.200g (51%) of **2a** was isolated as a colorless gum. Spectral data for poly(alcohol)s (**2a**-**2i**) were identical with those shown in 3-1.

References

1) Pelter, A.; Smith, K.; Brown, H. C. In *Borane Reagents*; Academic Press: London, 1988, p272, and references cited therein.
2) See references in 3-1.

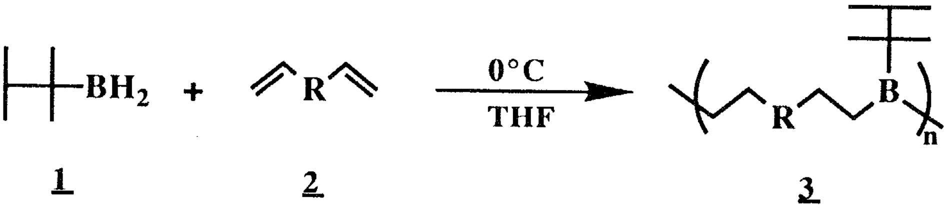
3 - 4

Synthesis of Poly(alcohol)s Having Primary and Tertiary Hydroxyl Groups by the Reaction with α-Furyllithium.

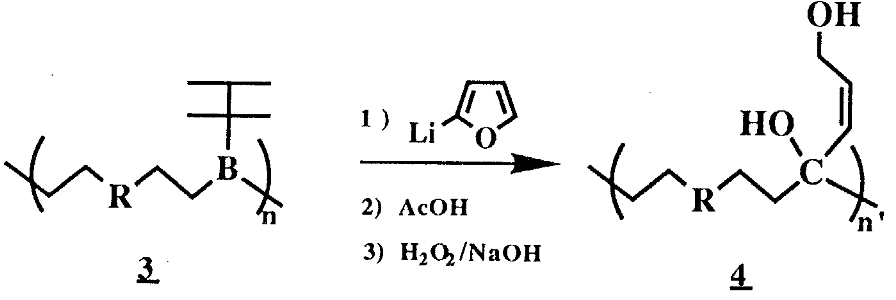
Introduction

As described in Chapter 1, organoboron polymers were prepared by a novel polyaddition reaction between monoalkylborane and bifunctional monomers such as dienes and diynes (i.e., "Hydroboration Polymerization", Scheme I). Although, Chung *et al.* reported that polymers having organoboron branches were transformed to structurally well defined poly(alcohol)s1), the resulting polymers always have functional groups in their side chains. As the organoboron polymers prepared by hydroboration polymerization have reactive points in their main chains, they may serve as precursors to offer the novel materials bearing functional groups in their main chains.

Scheme I



Scheme II

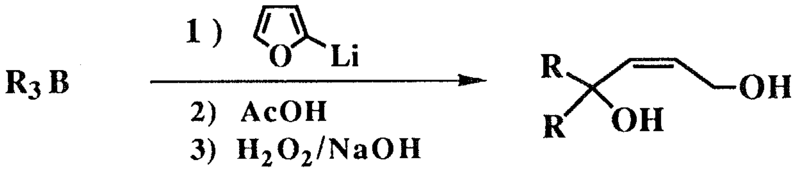


The direct applications of versatile reactions reported in the field of organoborane chemistry may expand the synthetic methodology to produce novel functional polymers starting from the organoboron polymers. As to explore the possibilities for the novel polymer conversion reactions, this chapter deals with the synthesis of poly(alcohol)s having primary and tertiary hydroxyl groups by the reactions of organoboron polymers with α-furyllithium (Scheme II).

Results and Discussion

According to the previous papers[2)], the reactions between organoboron compounds and α-furyllithium followed by the oxidative treatment with alkaline hydrogen peroxide, gave the corresponding 4,4-dialkyl-*cis*-2-butene-1,4-diols, as shown in Scheme III. In this reaction, two alkyl groups in trialkylborane participate in the migration reaction. In the case of dialkylthexylborane, selective migration of two alkyl groups without that of thexyl group in the organoborane unit might be expected[3)]. Thus, selective migration of primary alkyl groups in the organoboron polymer unit (i.e., main chain of the polymer) may realize the conversion reaction of polymer structure without obvious scission of the main chains.

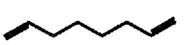
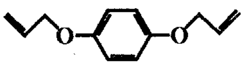
Scheme III



The starting organoboron polymers (**3a**-**3c**) were prepared easily by the reactions of thexylborane (**1**) with various dienes (**2a**-**2c**), respectively[4)] (Scheme I), and were used for the reactions with α-furyllithium without isolation. The molecular weights of **3a**-**3c** and **4a**-**4c** were determined by GPC[4)] using THF as an eluent. The results are summarized in Table I. From the result, M_n of the product poly(alcohol)s (**4**) were almost the same as those of starting organoboron polymers (**3**).

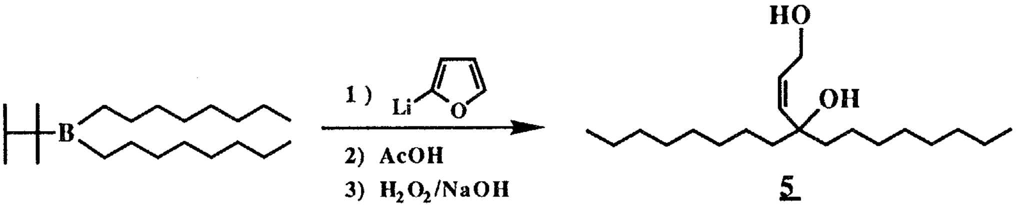
As to get an information of polymer structures and of reaction itself, a model reaction was carried out using dioctylthexylborane in place of an organoboron polymer (Scheme IV). The structure of the product (5) was confirmed by its ^{1}H-NMR. As shown in Figure 1, the peaks corresponding to olefinic protons and methylene protons adjacent to hydroxyl groups were observed around 5-6 and 4.4 ppm, respectively. The integral ratios between olefinic protons and others were found to be in good agreement with the calculated values for the expected structure. This result indicates that this reaction only accompanies a migration of a primary alkyl group rather than a tertiary one.

Table I Synthesis of Poly(alcohol)s from Various Organoboron Polymers.

Run	Diene (2)	B-Polymer (3)	Poly(alcohol) (4)	
		$M_n^{a)}$	$M_n^{b)}$	$M_w^{b)}$
1	 (a)	3,970	2,890	6,750
2	 (b)	1,280	1,330	2,620
3	 (c)	1,190	1,200	2,020

a) GPC (dry THF), polystyrene standard. b) GPC (THF), polystyrene standard.

Scheme IV



^{1}H-NMR spectrum of **4a** is shown in Figure 2. The olefinic protons and methylene protons adjacent to hydroxyl groups were observed in the same region as for the model compound (**5**). The presence of large peak around 0.5-1.0ppm, however, indicates that either the obtained poly(alcohol) was still contaminated with some impurities containing thexyl groups or the structure of the obtained polymer was not the proposed one. The integral ratio of this peak to those of olefinic protons was much higher than the expected ratio for the thexyl groups at the polymer ends on the basis of the number-average molecular weight in GPC. Namely, the peak around 0.5-1.0ppm for thexyl group was found to decrease by the successive reprecipitations with *n*-hexane. Therefore, the insufficient result in ^{1}H-NMR spectrum can be explained by the contaminated impurities which contain thexyl groups. Though the impurities in the obtained product could be removed by the successive reprecipitation with *n*-hexane, this method was not suitable for the purification of the present polymer due to the low efficiency for the polymer recovery. Several trials to isolate the polymer were not successful possibly due to the strong coordination between impurities and polymer chains by means of boronic acid derivatives.

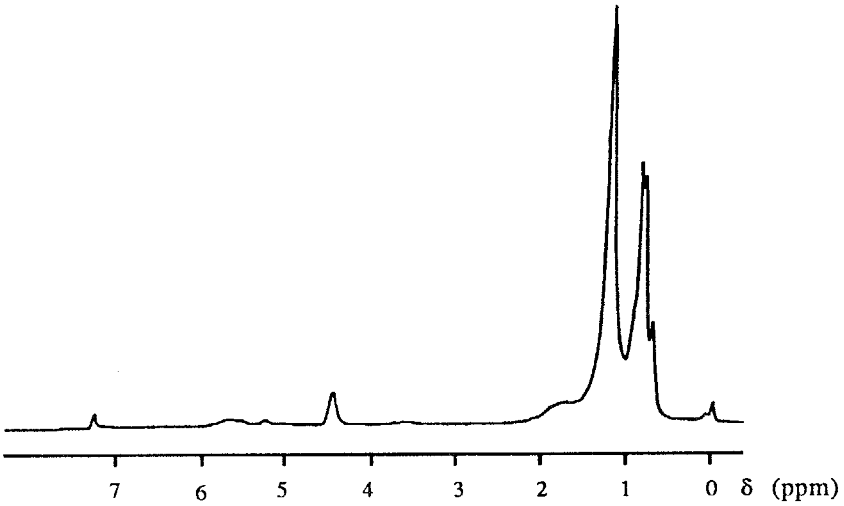


Figure 1 ^{1}H-NMR spectrum of **5**.

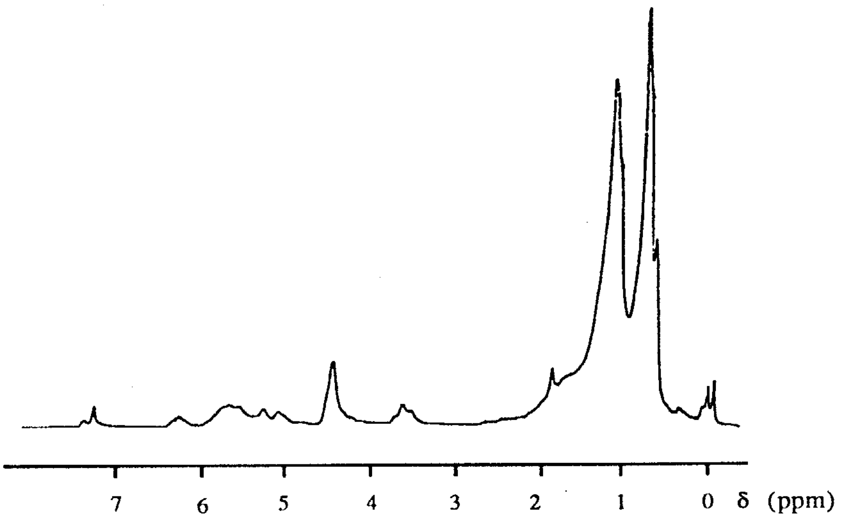
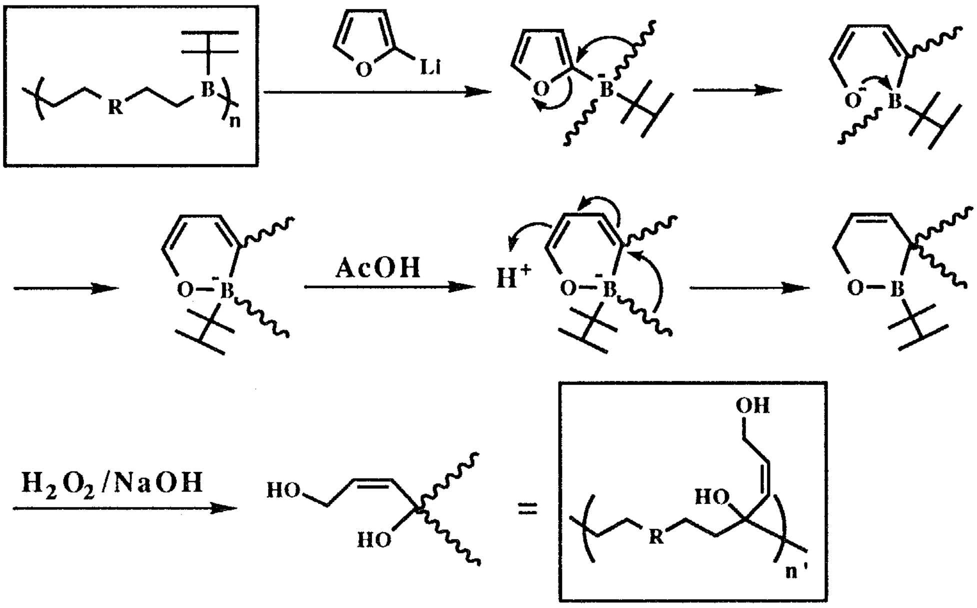


Figure 2 ^{1}H-NMR spectrum of **4a**.

Referred to the proposed mechanism for the reaction of trialkylborane with α-furyllithium, the present polymer reaction can be considered to proceed as shown in Scheme V. That is, the reaction of **3** with α-furyllithium affords lithium 2-furyltrialkylborate, in which one polymer chain migrates from boron atom to α-carbon of furan ring, accompanied with its ring-opening. Then, the coordination of oxygen atom to boron atom gave the six-membered cyclic borate[5]. After the migration of another polymer chain by means of proton, the corresponding cyclic borate produced the aiming poly(alcohol) *via* the ring-opening of the cyclic borate by the treatment with alkaline hydrogen peroxide.

Scheme V



As mentioned above, primary alkyl groups are generally more reactive than tertiary alkyl groups in this type of anionic intramolecular rearrangement. Accordingly, it is reasonable to suppose that the migration of the main chains in the polymer (mainly consist of primary alkyl groups) rather than that of thexyl group (tertiary alkyl group) is more feasible in the present reaction. The large different reactivity should make it possible to convert the polymer structure without obvious scission of the main chain.

Experimental Section

Materials and Instruments. **1** was prepared by the reaction of borane-dimethyl sulfide complex with 2,3-dimethyl-2-butene⁶⁾ and was purified by distillation⁴⁾. 1-Octene, **2a** and **2b** were purified by distillation. **2c** (prepared from hydroquinone and allyl bromide⁴⁾) was purified by recrystallization from *n*-hexane. Acetic acid was purified by distillation after refluxing with acetic anhydride. Diethyl ether and tetrahydrofuran were dried over sodium and distilled before use. *n*-Butyllithium, sodium hydroxide, hydrogen peroxide (30%), *n*-hexane, and benzene were used without further purification.

^{1}H-NMR spectra were recorded in $CDCl_3$ on a Hitachi R-600 instrument. IR spectra were obtained on a Perkin Elmer 1600 spectrometer. Gel permeation chromatographic analyses were carried out on a Tosoh HLC-8020 (TSK gel G4000) after calibration with standard polystyrene samples.

Synthesis of Diol (5) by the Reaction of Dioctylthexylborane with α-Furyllithium (A Model Reaction). A 30ml round-bottomed flask equipped with a reflux condenser and a magnetic stirrer tip was flushed with nitrogen. The flask was charged with 0.27ml (3.71mmol) of furan, which was treated with 2.5ml of 1.6M *n*-butyllithium/*n*-hexane in 5ml of diethyl ether. The mixture was kept under stirring at reflux for 6h. Then, a THF solution of dioctylthexylborane, prepared from 0.2ml of thexylborane (1.55mmol) and 0.8ml of 1-octene in THF at 0°C and isolated by vacuum drying, was added to the solution of α-furyllithium gradually at room temperature by a syringe. After stirring overnight, 0.3ml of acetic acid was added to the reaction mixture followed by the treatment with 3ml of 1N sodium hydroxide and 1ml of 30% hydrogen peroxide for 5h. The mixture was extracted with diethyl ether, and the combined extracts were dried over sodium sulfate and concentrated by vacuum drying. ^{1}H-NMR (δ, ppm) 0.86 (CH_3, t, 6H), 1.17-2.70 (CH_2, m, 14H), 4.28-4.56 (OCH_2, m, 2H), 4.90-5.93 (C=CH, m, 2H).

Synthesis of Poly(alcohol)s (4a-4c) by the Reactions of Organoboron Polymers (3a-3c) with α-

Furyllithium. A typical procedure is shown as follows: **3a**, prepared by the reaction of **2a** (0.141g, 1.28mmol) with thexylborane (0.167ml, 1.28mmol) in THF at 0°C, was reacted under the same conditions as mentioned in the part of Model Reaction. The product (**4a**) was dissolved in diethyl ether, precipitated into *n*-hexane and freeze-dried from benzene. ^{1}H-NMR spectrum is shown in R&D section. **4b** and **4c** were prepared in a similar manner.

References and Notes

1) a) Chung, T. C.; Roate, M.; Berluche, E.; Schulz, D. N. *Macromolecules*, **1988**, 21, 1903. b) Chung, T. C. *J. Polym. Sci., Polym. Chem. Ed.*, **1989**, 27, 3251. c) Ramakrishnan, S.; Chung, T. C. *Macromolecules*, **1989**, 22, 3181. d) *Idem. J. Organomet. Chem.*, **1990**, 388, 1. e) Ramakrishnan, S.; Berluche, E.; Chung, T. C. *Macromolecules*, **1990**, 23, 378. f) Ramakrishnan, S.; Chung, T. C. *ibid.*, **1990**, 23, 4519. g) Chung, T. C.; Rhubright, D. *ibid.*, **1991**, 24, 970. h) Chung, T. C.; Ramakrisnan, S.; Kim, M. K. *ibid.*, **1991**, 24, 2675.
2) Suzuki, A.; Miyaura, N.; Itoh, M. *Tetrahedron*, **1971**, 27, 2775.
3) In a series of various intramolecular migrations of organoboron compounds, selectivity between primary and tertiary alkyl group has been reported. See the references cited in Sections 1-3.
4) See 2-1.
5) The cyclic borate was isolated by column chromatography in ref. 2), from which the proposed mechanism was supported.
6) Brown, H. C.; Mandal, A. K.; Kulkarni, S. U. *J. Org. Chem.*, **1977**, 42, 1392.

3 - 5

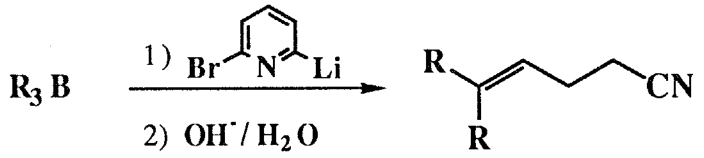
Synthesis of Nitrile-Containing Polymers by the Reaction with 2-Bromo-6-lithiopyridine.

Introduction

In Chapter 2, the author has described the synthesis of polymers having organoboron moieties in the main chain. These polymers can be converted to various functional polymers as mentioned in Sections 1-4. Especially, the organoboron polymers obtained by hydroboration polymerization between diene and monoalkylborane can be regarded as a polymer homologue of trialkylborane. Thus, they may be expected to have a potential as a novel reactive polymer, in which reactive points are located in the main chain.

In the field of organoboron chemistry, the reaction of trialkylboranes with 2-bromo-6-lithiopyridine followed by the treatment with sodium hydroxide is known to give the corresponding γ,δ-unsaturated nitriles[1] as shown in Scheme I.

Scheme I



An application of this migration reaction to organoboron polymers obtained by hydroboration polymerization may make it possible to prepare polymers bearing nitrile groups in the side chain.

Results and Discussion

The starting organoboron polymers (**3a**-**3g**) were prepared by the reactions of thexylborane (**1**) and various dienes (**2a**-**2g**), respectively, and were used for the reactions with 2-bromo-6-

lithiopyridine without isolation. As the result of the conversion reaction, polymers bearing carbon-carbon double bond and nitrile group in the pendant (4) were obtained, as shown in Scheme II.

Scheme II

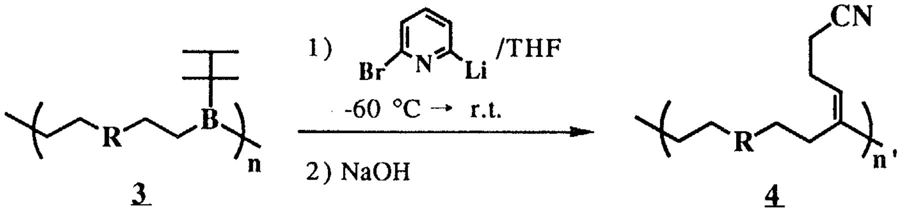
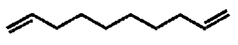
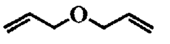
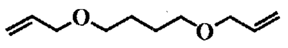
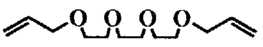
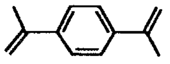


Table I Synthesis of Nitrile-Containing Polymers from Various Organoboron Polymers.

Run	Diene (2)		3	4		
			M_n^a)^	M_n^b)^	M_w^b)^	Yield(%)^c)^
1		(a)	3,420	3,980	7,500	72
2		(b)	3,120	2,990	4,910	57
3		(c)	680	1,090	1,950	17
4		(d)	2,670	2,200	2,760	59
5		(e)	1,240	1,570	2,120	80
6		(f)	1,970	1,490	2,940	71^d)^
7		(g)	1,670	1,020	1,400	79^d)^

a) GPC(dry THF), polystyrene standard. b) GPC(THF), polystyrene standard.
c) Isolated yields after reprecipitations into Et_2O/*n*-hexane (v/v=1/4).
d) Isolated yields after reprecipitations into $MeOH/H_2O$(v/v=1/1).

The molecular weights of the starting organoboron polymers (**3a**-**3g**) and the resulting polymers (**4a**-**4g**) were determined by GPC using THF as an eluent2) (Table I). Under the same conditions reported for trialkylboranes1), **4a**-**4g** obtained had almost the same molecular weights as those of starting polymers (**3a**-**3g**, respectively). For example, the number-average molecular weights of **3a** and **4a** were 3,420 and 3,980, respectively.

The structures of the resulting nitrile-containing polymers thus obtained were characterized by spectroscopic analyses such as ^{1}H-, ^{13}C-NMR and IR. ^{1}H-NMR and IR spectra of **4a** are shown in Figure 1 and Figure 2, respectively.

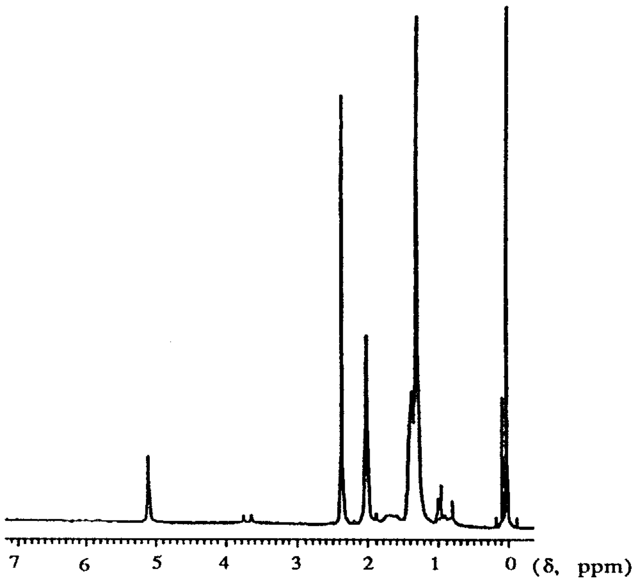


Figure 1 ^{1}H-NMR spectrum of 4a.

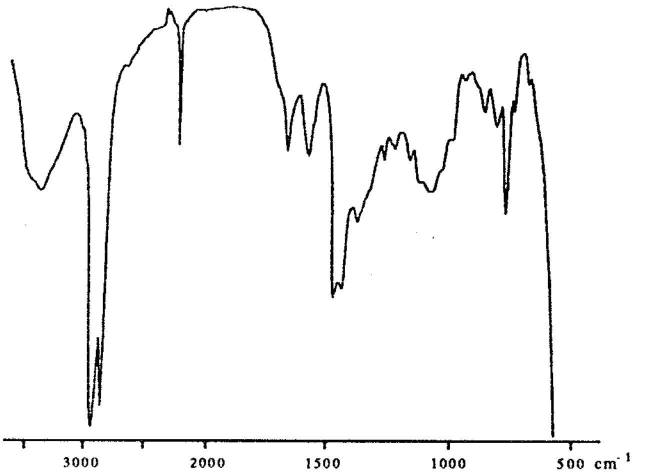
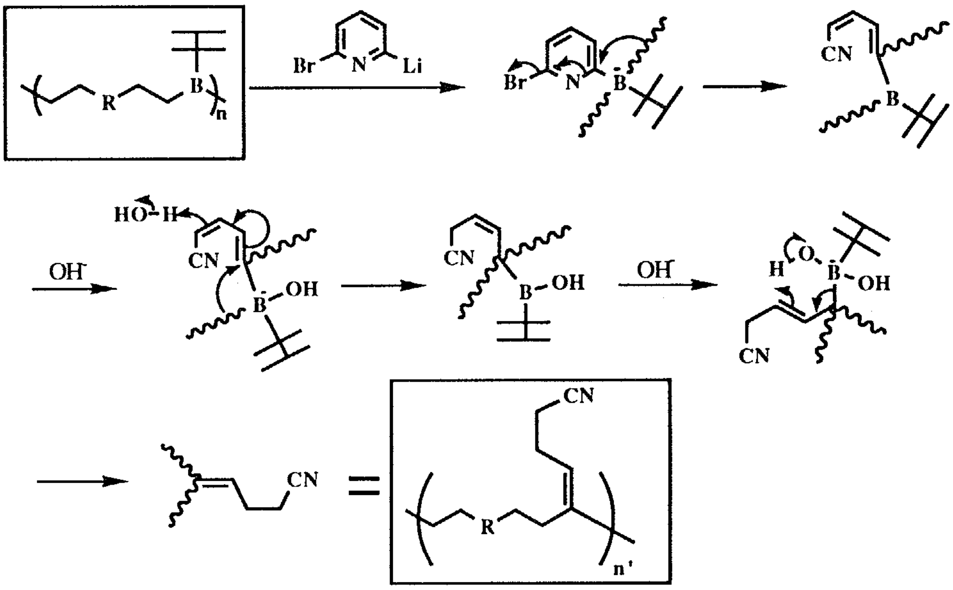


Figure 2 IR spectrum of 4a.

In Figure 1, the peak due to olefinic proton was observed around 5.1ppm, and the integral ratio between olefinic proton and others was in good agreement with the calculated value for the expected structure. Small peaks around 1.0ppm were also observed probably due to the remained thexyl protons at the polymer ends (or impurities). In the IR spectrum of **4a**, two absorption bands assignable to C≡N and C=C stretching vibrations were observed around 2246 and 1665cm^{-1}, respectively (Figure 2). The spectroscopic analyses of other polymers (**4b**, **4d**-**4g**) also confirmed their structures. In the case of **3c**, however, the resulting polymer (**4c**) having low molecular weight was isolated in a low yield due to the insufficient molecular weight of the starting **3c**.

Referred to the proposed mechanism for the reaction of trialkylboranes with 2-bromo-6-lithiopyridine, the present polymer reaction may proceed as shown in Scheme III. That is, the reaction of **2** with 2-bromo-6-lithiopyridine affords lithium (6-bromo-2-pyridyl)trialkylborate, in which one polymer chain migrates from boron to α-carbon of pyridine ring, accompanying the ring-opening of pyridine ring and the elimination of bromide anion. Two following generations of borate anions and migrations of alkyl groups give rise to the nitrile-containing polymers. Generally, a primary alkyl group is said to be more reactive than a tertiary alkyl group in this intramolecular rearrangement. Accordingly, it is reasonable to suppose that the migration of the polymer chains is easier than that of thexyl group, since polymer chains of organoboron polymer consist of primary alkyl groups. Similarly to the results described in Sections 1-4, this different reactivity should made it possible to obtain the resulting polymers without the decrease of molecular weight.

Scheme III



Generally, it might be difficult to prepare nitrile-containing polymers by means of conventional polymer synthetic methods. Thus, the present study provides a useful and convenient method for the preparation of polymers having nitrile groups. In other words, organoboron polymers prepared by hydroboration polymerization can be expected as a novel type of reactive polymers.

Experimental Section

Materials and Instruments. **1** was prepared by the reaction of borane-dimethyl sulfide complex with 2,3-dimethyl-2-butene[3] and was purified by distillation. 2,6-Dibromopyridine was purified by recrystallization from THF/*n*-hexane. Tetrahydrofuran was dried over sodium and distilled before use. *n*-Butyllithium, sodium hydroxide, hydrogen peroxide (30%), benzene, diethyl ether, *n*-hexane and methanol were used as received.

^{1}H-NMR spectra were recorded in $CDCl_3$ on a Hitachi R-600 instrument or JEOL LNM-GX400 instrument. ^{13}C-NMR spectra were recorded in $CDCl_3$ on a Hitachi R-900 instrument. IR spectra were obtained on a Perkin Elmer 1600 spectrometer. Gel permeation chromatographic analyses were carried out on a Tosoh HLC-8020 (TSK gel G4000) after calibration with standard polystyrene samples.

Synthesis of Nitrile-Containing Polymers (4a-4g) from Organoboron Polymers (3a-3g). A typical procedure is described as follows: The organoboron polymer (**3a**) was prepared by polyaddition between **1** (0.127g, 1.30mmol) and **2a** (0.145g, 1.31mmol), as shown in 2-1. 2-Bromo-6-lithiopyridine was prepared from 2,6-dibromopyridine (0.370g, 1.56mmol) and *n*-butyllithium (1.6N in *n*-hexane, 0.98ml, 1.57mmol) in diethyl ether (3.0ml) as reported earlier[1]. To the solution of 2-bromo-6-lithiopyridine, a THF solution (3ml) of **3a** was added at -60°C under nitrogen. The mixture was gradually warmed to room temperature and was kept stirring overnight, followed by the addition of aqueous sodium hydroxide (1N, 6ml). After stirring overnight, this mixture was extracted with diethyl ether, dried over sodium sulfate, and concentrated. The crude material was reprecipitated into diethyl ether/*n*-hexane (v/v=1/4) followed by freeze-drying to give a brown gum. Yield 72%; ^{1}H-NMR (δ, ppm) 1.07-1.46 (CH_2, m, 12H), 1.89-2.11 ($C=C-CH_2$, m, 4H), 2.28-2.44 (CH_2CH_2CN, m, 4H), 5.04-5.16 (C=CH, m, 1H); ^{13}C-NMR (δ, ppm) 17.4, 23.9, 28.2, 29.4, 30.2, 36.8, 119.1, 119.8, 143.8; IR (film) 2921, 2856, 2246, 1665, 1572, 1464, 1425, 1365, 1071, 755cm^{-1}.

Various nitrile-containing polymers were prepared in a similar manner as mentioned above. **4f** and **4g** were precipitated into MeOH/H_2O (v/v=1/1). **4b**: Yield 57%; ^{1}H-NMR (δ, ppm) 0.97-1.67 (CH_2, m, 16H), 1.67-2.17 ($C=C-CH_2$, m, 4H), 2.17-2.47 (CH_2CH_2CN, m, 4H), 4.87-5.27 (C=CH, m, 1H); IR (film) 2921, 2856, 2246, 1665, 1583, 1464, 1262, 1164, 1066, 799cm^{-1}. **4d**: Yield 59%; ^{1}H-NMR (δ, ppm) 1.27-2.17 (CH_2, m, 12H), 2.17-2.52 (CH_2CH_2CN, m, 4H), 2.92-4.11 (OCH_2, m, 8H), 4.87-5.33 (C=CH, m, 1H); ^{13}C-NMR (δ, ppm) 17.3, 23.4, 25.7, 27.6, 69.5, 118.8, 120.2, 141.7; IR (film) 3019, 2965, 2921, 2867, 2246, 1660, 1578, 1453, 1431, 1376, 1262, 1218, 1158, 1088cm^{-1}. **4e**: Yield 80%; ^{1}H-NMR (δ, ppm) 1.30-2.15 (CH_2, m, 8H), 2.15-2.47 (CH_2CH_2CN, m, 4H), 2.80-4.07 (OCH_2, m, 16H), 4.87-5.25 (C=CH, m, 1H). **4f**: Yield 71%; ^{1}H-NMR (δ, ppm) 1.03-1.62 (CH_3, d, 6H), 1.65-2.45 (CH_2, m, 8H), 2.45-3.35 (CH, m, 2H), 4.81-5.58 (C=CH, m, 1H), 6.65-7.20 (C_6H_4, m, 4H); IR (film) 3019, 2965, 2246, 1660, 1600, 1578, 1453, 1371, 1218, 1093, 891, 755cm^{-1}. **4g**: Yield 79%; ^{1}H-NMR (δ, ppm) 1.37-2.87 (CH_2, m, 12H), 3.48-4.15 (OCH_2, m, 4H), 4.77-5.32 (C=CH, m, 1H), 6.30-6.95 (C_6H_4, m, 4H); IR (film) 3052, 2921, 2867, 2246, 1583, 1551, 1507, 1464, 1420, 1229, 1109, 1055, 913, 826cm^{-1}.

References

1) Utimoto, K.; Sakai, N.; Obayashi, M.; Nozaki, H. *Tetrahedron*, **1976**, 32, 769.

2) The molecular weights of **3a**-**3g** were measured by GPC using dried THF as an eluent with a constant nitrogen bubbling. For details, See 2-1.

3) Brown, H. C.; Mandal, A. K. ; Kulkarni, S. U. *J. Org. Chem.*, **1977**, 42, 1392.

Chapter 4

Synthesis of Novel Boron-Containing Polymers by Hydroboration Polymerization of Dicyano Compounds

ABSTRACT

A new methodology for the preparation of "Air-Stable Boron-Containing Polymers" by the polyaddition between dicyano compounds and monoalkylboranes or dialkylboranes is described.

In 4-1, t-$BuBH_2 \cdot NMe_3$ was used as a monoalkylborane part, and the polyaddition with several kinds of dicyano monomers was examined. From the stoichiometric study using isophthalonitrile as a dicyano monomer, a small excess amount of borane was found to increase the molecular weight of the obtained polymer in this polymerization. The structure of the resulting polymer was confirmed by ^{1}H-, ^{13}C-, ^{11}B-NMR, UV, and IR analyses. The stability of the boron-containing polymer against air and moisture as well as thermal stability was examined. The boron-containing polymer was found to be stable under air and moisture. As a dicyano compound, terephthalonitrile, 1,5-di(4,4'-cyanophenoxy)pentane and α,ω-dicyanoalkanes were also used in the present hydroboration polymerization. Among these compounds, the monomers having aromatic cyano groups rather than aliphatic ones gave polymers with higher molecular weights.

In 4-2, steric effects of the alkyl substituents on the monoalkylborane monomers were examined. When less sterically hindered monoalkylboranes such as n-$BuBH_2 \cdot NMe_3$ and i-$PrBH_2 \cdot NMe_3$ were used as a monomer, less soluble materials were obtained due to the cross-linking reaction. From the reaction using thexylborane, however, α,ω-dicyanoalkanes rather than aromatic ones gave soluble oligomers. The results obtained in Sections 1 and 2 indicated that monoalkylboranes having tertiary alkyl groups are suitable for the present polymerization with aromatic dicyano monomers. For the aliphatic monomers, more hindered tertiary alkyl groups are required to prevent the dihydroboration reaction (i.e., attacks of B-H towards iminoboranes).

In 4-3, dialkylborane was used as a monomer instead of monoalkylboranes. The bulk polymerization of $(n\text{-}Bu_2BH)_2$ with α,ω-dicyanoalkanes gave the corresponding polymers as colorless gums within several hours' reaction in bulk. The obtained

polymers were stable under air, and the molecular weights of the resulting polymers were higher than those from monoalkylboranes.

In a practical point of view, preparation and isolation of dialkylboranes are difficult due to their instability. Therefore, in 4-4, dialkylborane monomers were prepared *in situ* by the *retro*-hydroboration reaction of thexyldialkylborane prepared from thexylborane and the corresponding terminal olefins. The structures of the polymers obtained in the present method were identical with those prepared from isolated dialkylborane and dicyano monomers. By using this method, dialkylboranes with longer alkyl chains could be also utilized as monomer components.

The polymers prepared by hydroboration polymerization of dicyano compounds in this chapter were stable under air and gave some residue after pyrolysis. These results may open a useful way to obtain boron-containing inorganic materials.

4 - 1

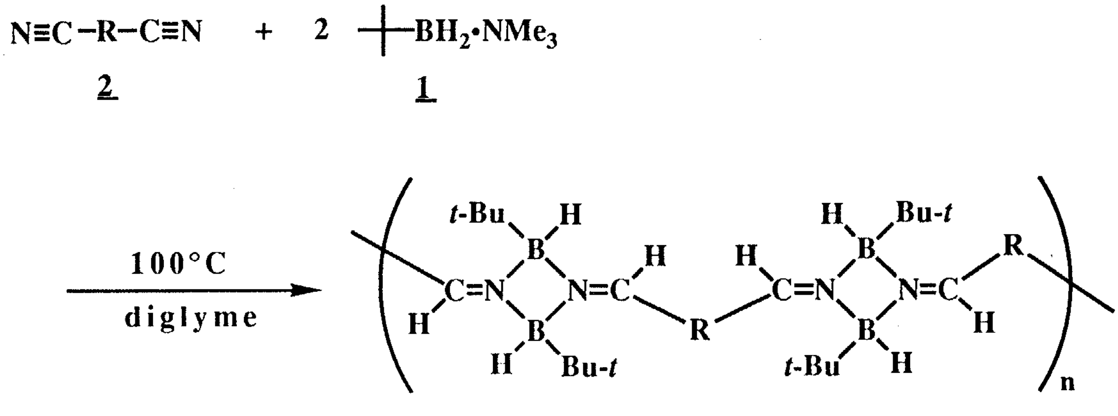
Synthesis of Boron-Containing Polymers by the Reaction between t-BuBH$_2$•NMe$_3$ and Dicyano Compounds.

Introduction

In Chapter 2 of this thesis, synthesis of novel organoboron polymers by the novel step-growth polymerization reaction, that is, "Hydroboration Polymerization" is described. For example, polyaddition between dienes and thexylborane by means of hydroboration gave the corresponding organoboron polymers1), which were proved to have the interesting characteristics as novel reactive polymers to produce various kinds of polymers having functional groups2). Poly(organoboron halide)s formed by the polyaddition between boron tribromide and terminal diynes were also found to have novel reactivities as a poly(Lewis acid) that will be also described in the later chapter of this thesis3).

On the other hand, the preparation of stable boron-containing polymers has been an attractive target because a few examples such as borazine, phosphinoborane, and decarborane polymers4) have been reported as the polymeric materials or as the precursors of inorganic materials5) after pyrolysis.

Scheme I



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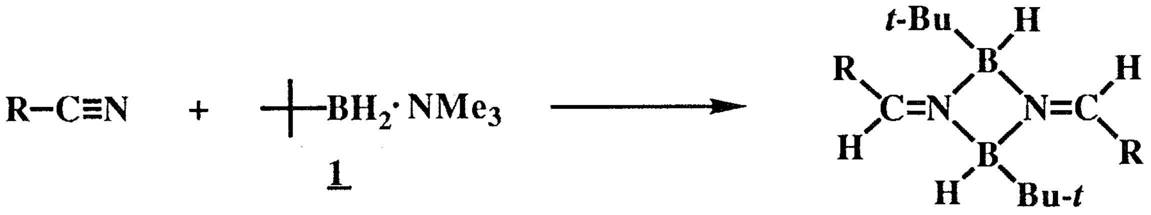
Here, the author describes a novel method to obtain air-stable boron-containing polymers by the polyaddition between dicyano compounds and *tert*-butylborane-trimethylamine (**1**) (Scheme I). The resulting boron-containing polymers having cyclodiborazane backbones (i.e., boron-nitrogen four-membered rings) were found to be stable enough under air and moisture.

Results and Discussion

According to a previous report by Hawthorne6), the reaction between **1** and various nitrile compounds results mainly in the formation of iminoborane dimers, i.e., cyclodiborazanes (Scheme II).

Scheme II



The formation of these boron-nitrogen four-membered rings was reported also in the cases of the reactions between allylboranes and nitriles7), thioesters of dialkylboronic acids and imines8), tetraalkyldiborane and nitrile9), and so on10). These compounds were reported to be stable enough against air and moisture. This fact may indicate the possibility to build up a boron-containing polymer having this structure. In this chapter, polyaddition by using the reaction reported by Hawthorne6) was examined with bifunctional dicyano compounds.

Hydroboration Polymerization between 1 and Isophthalonitrile (2a). As a preliminary example, polymerization of **2a** with **1** was examined to optimize the reaction conditions. All the reactions were carried out in a diglyme solution under nitrogen atmosphere. The molecular weights of the resulting polymers were measured by GPC (THF as an eluent) after calibration with standard polystyrenes. The results are summarized in Table I. In runs 1, 2, and 5, the effect of reaction temperature was examined. From these results, polymerization at 100°C was shown to be the best condition. In order to obtain the moderate reactivity from **1**, it is required to remove trimethylamine ligand by means of heating. At 120°C, however, the resulting polymer seemed to contain another structure[11], possibly due to the undesirable side reaction. As a result, when the reaction was carried out at 140°C, gelation was observed. The reaction time was varied at 100°C (runs 2-4), from which the decomposition of the polymer was observed after a longer heating (*vide infra*). When the reaction mixture (run 2) was precipitated into EtOH/H_2O (v/v=1/1), a white solid was obtained in a 96% yield. The obtained polymer (**3a**) was soluble in various organic solvents such as THF, CH_2Cl_2, $CHCl_3$, and benzene.

Table I Polymerization Conditions between 1 and 2a[a].

Run	$\frac{[t\text{-}BuBH_2NMe_3]}{[C{\equiv}N]}$ Ratio	Reaction Conditions	$\overline{M}_n$[b]	$\overline{M}_w$[b]	Yield[c] (%)
1	1.02	80°C 1h	1,240	1,990	-
2	0.99	100°C 1h	4,030	6,140	96
3	1.05	100°C 2h	1,320	2,170	-
4		100°C 4.5h	550	690	-
5	0.98	120°C 1h	3,680	12,600	93

a) Reactions were carried out in diglyme.
b) GPC, polystyrene standard.
c) Isolated yield after precipitation into EtOH/H_2O (v/v=1/1).

The dependence of molecular weight on the feed ratio between the two monomers (**1**/**2a**) was examined. As is shown in Table II and Figure 1, with increasing the feed ratio of **1**/**2a**, the molecular weight of the resulting polymer increased. It was found that the polymerization with a small excess amount of **1** gave a polymer having higher molecular weight than that with a stoichiometric amount of **1** (run 4 vs. 5). However, further excess amount of **1** gave no more effect on the molecular weight (runs 6 and 7).

Table II Effect of feed ratio of 1/2a[a)].

Run	$\frac{[t\text{-BuBH}_2\text{NMe}_3]}{[\text{C≡N}]}$ Ratio	$\overline{M}_n$ b)	$\overline{M}_w$ b)	Yield c) (%)
1	0.32	500	680	-
2	0.49	870	1,250	-
3	0.82	1,630	3,320	-
4	0.99	4,030	6,140	96
5	1.55	7,590	27,200	96
6	2.17	6,610	26,000	96
7	2.97	7,080	30,300	98

a) Reactions were carried out in diglyme.
b) GPC, polystyrene standard.
c) Isolated yield after precipitation into $EtOH/H_2O$ (v/v=1/1).

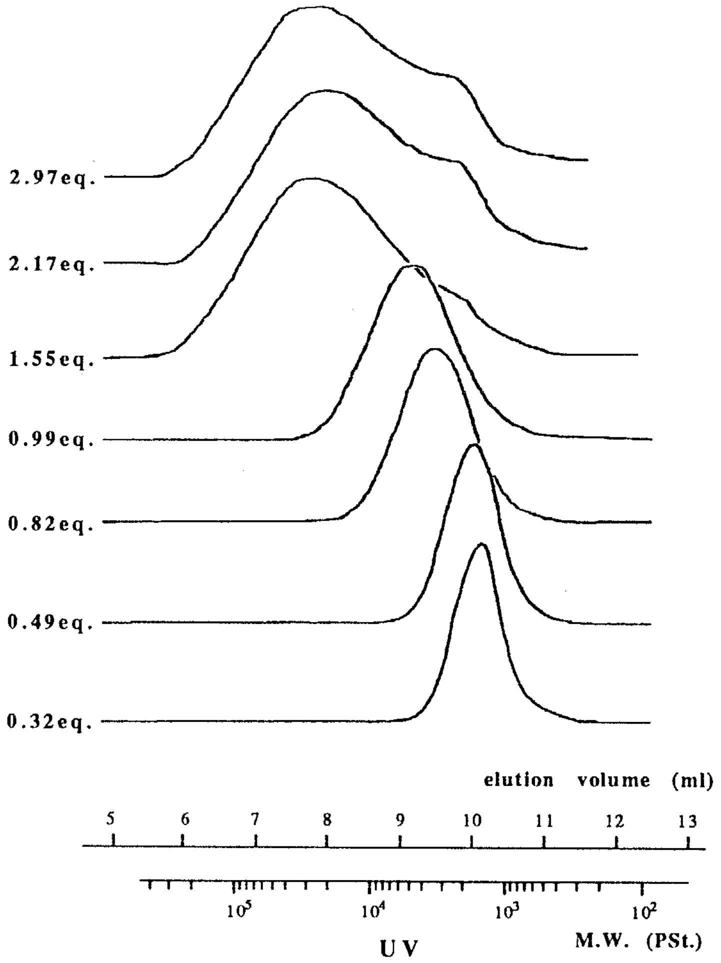
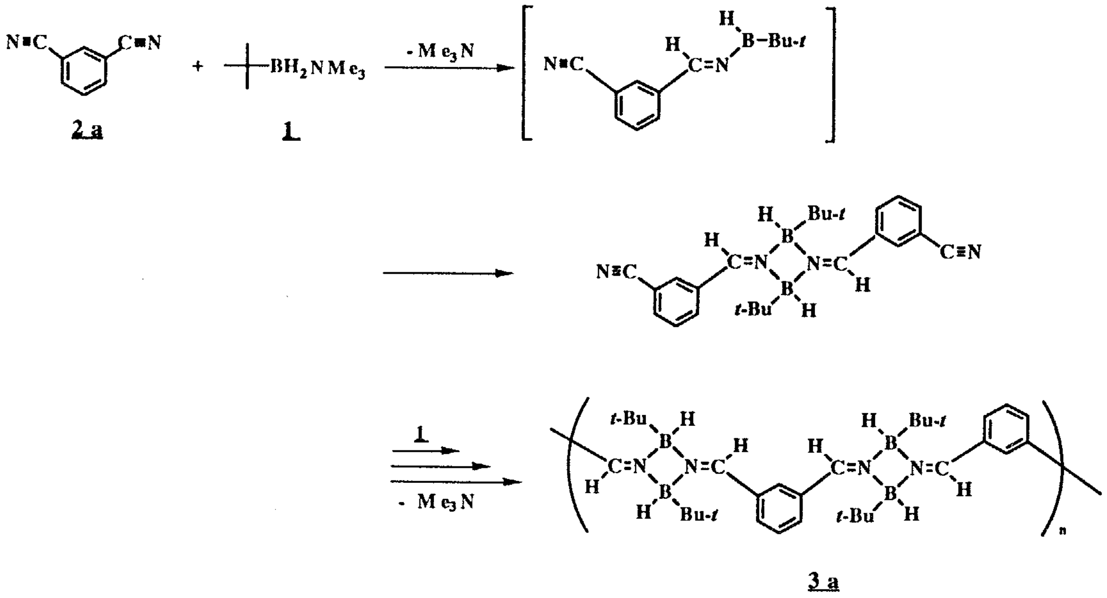


Figure 1 Dependence of molecular weight of 3a on the feed ratio of the monomers (1/2a).

Polymerization should proceed as illustrated in Scheme III. Accordingly, the formation of iminoborane species should be essential for this polymerization. On the assumption that the iminoborane species never reacts further with an excess of **1**, the higher conversion of the nitrile group into iminoborane should be favorable for this polymerization, which is considered to be achieved by using a small excess amount of **1**. This assumption was confirmed by a model reaction between **1** and benzonitrile (**4**) as well as by the comparison of spectroscopic data of obtained polymers varying the feed ratio of **1**/**2a** (*vide infra*).

Scheme III



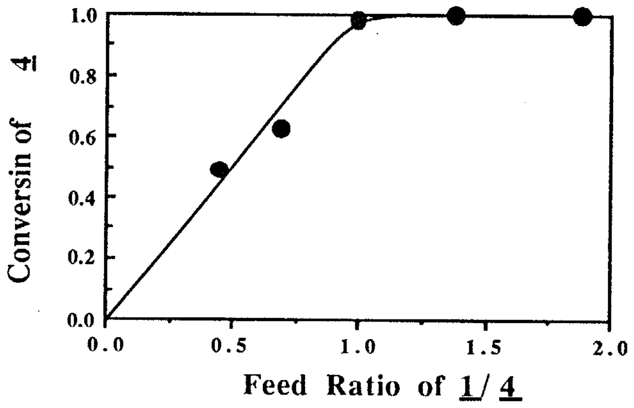
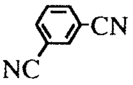
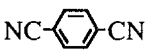
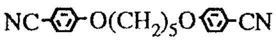


Figure 2 GC conversion curve of 4 by the reaction with 1.

The conversion curve of **4** followed by GC analysis is shown in Figure 2. It is seen that a small excess amount of **1** brings about a quantitative conversion of **4**. When two fold excess of **1** was reacted with **4**, the aiming product (**5**) was isolated in the yield of 90%[12]. This finding is taken to rationalize the improved result of polymerization with an excess amount of **1**.

Hydroboration Polymerization of Various Dicyano Compounds. The present hydroboration polymerization was also examined using various dicyano compounds. The results are summarized in Table III. Instead of **2a**, terephthalonitrile (**2b**) and 1,5-di(4,4'-cyanophenoxy)pentane (**2c**) also gave the corresponding polymers (**3b**, **3c**, respectively) whose M_n was found to be 3,280 and 6,440, respectively, when small excess of **1** was used.

Table III Synthesis of Boron-Containing Polymers from Various Dicyano Compounds and 1.[a]

Run	Dicyano Compound		$\frac{[t\text{-BuBH}_2\text{NMe}_3]}{[\text{C}{\equiv}\text{N}]}$ Ratio	$\overline{M}_n$[b]	$\overline{M}_w$[b]	Yield[c] (%)
1		(2a)	1.55	7,590	27,200	96
2		(2b)	1.94	3,280	12,000	84
3		(2c)	1.73	6,440	21,400	93
4[d]	$NC(CH_2)_4CN$	(2d)	0.89	810	1,380	-
5[d]			1.65	300	400	-
6[d]	$NC(CH_2)_6CN$	(2e)	0.93	780	990	-
7[d]	$NC(CH_2)_8CN$	(2f)	1.03	750	1,710	-

a) Reactions were carried out at 100°C for 1h in diglyme.
b) GPC, polystyrene standard.
c) Isolated yield after precipitation into EtOH/H_2O (v/v=1/1).
d) GPC was measured without isolation.

Aliphatic dicyano compounds (**2d**-**2f**), however, resulted in the formation of oligomers with very low molecular weights. IR and ^{1}H-NMR spectra of **3d**-**3f** indicate that the further hydroboration reaction of iminoborane species did take place during the polymerization. By the Rimini test of the obtained oligomers, the presence of primary amine was also detected. This side reaction produced dibora-amine species, which should be readily cleaved during the measurement of the GPC. This is taken to be one of the reasons for the poor results with aliphatic dicyano compounds.

Characterization of Boron-Containing Polymers. Structure elucidation of **3a** was performed by comparison with spectroscopic data of model compound (**5**)6) in ^{1}H-, ^{13}C-, ^{11}B-NMR, UV, and IR spectra. In the IR spectrum of **3a**, the peaks due to B-H stretching (2350-2400cm^{-1}), and C=N stretching (1645cm^{-1}) were observed similarly to **5**. The relative intensities of the peaks for B-H, C≡N, and C=N of the boron-containing polymers prepared with some varied feeding ratios of **1**/**2a** are calculated to the peak at 1479cm^{-1} (Table IV). From these results, no decrease of C=N nor increase of B-H was observed even in the polymer prepared with 3eq. of **1**. Thus, this result is taken to mean that the iminoborane species is less reactive toward further hydroboration reaction. On the other hand, the disappearance of the peak for C≡N was observed when excess **1** was used. As mentioned above, these results indicate that excess of **1** only reacts with C≡N which brings about higher molecular weight polymers with the expected structure.

Table IV IR Data of the Boron-Containing Polymer (3a) Prepared under Various Conditions.

Sample	IR (cm^{-1})			
	2366 (νB-H)	2239 (νC≡N)	1645 (νC=N)	1479 (νC=C)
Table II, run 3	0.98	0.26	1.52	1
Table II, run 4	1.11	0.11	1.63	1
Table II, run 5	1.08	0	1.82	1
Table II, run 7	1.17	0	1.83	1
Table I, run 5	0.82	0.05	1.59	1

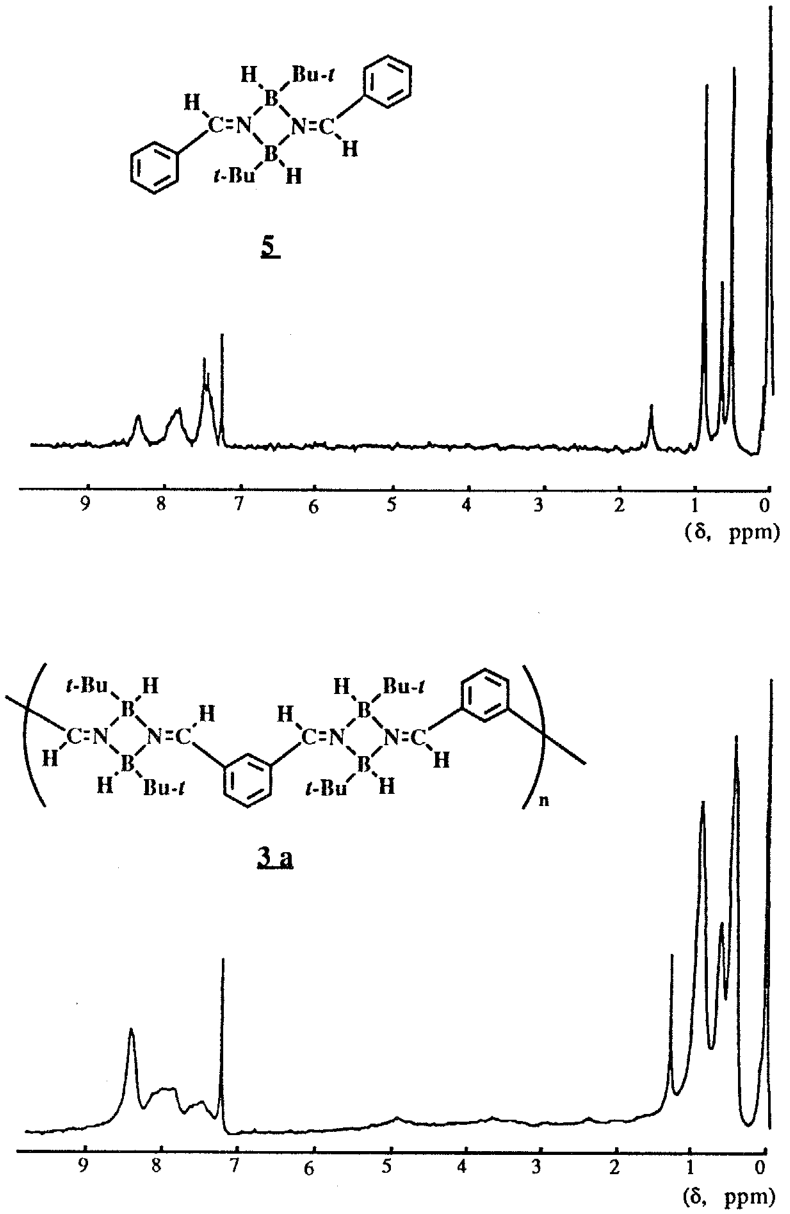
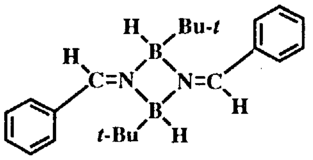
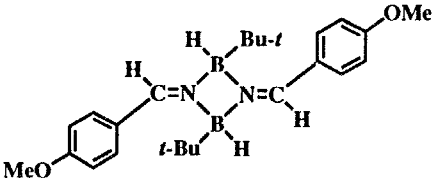


Figure 3 ^{1}H-NMR of the boron-containing polymer (3a) and a model compound (5).

In the ^{11}B-NMR of **3a** and **3c**, single broad peaks around -1.7ppm and 5.1ppm, respectively, were observed, which were close to the corresponding chemical shift for the model compound (**5**) (5.7ppm)[13]. In addition, these values are quite reasonable for the four coordinated boron species. In the UV spectrum, **3 a** showed an absorption maximum at 259nm, while **5** had absorption at 273nm (ε=11,400)[6]. The lower wavelength peak in the polymer can be ascribed to the torsion of the plane of the aromatic ring and the conjugated C=N bonds caused by the doubly attached *t*-butyl groups which is only effective for one *t*-butyl group per aromatic groups in the structure of **5**. As a fact, **3c** showed an absorption maximum at 302nm (in CH_2Cl_2), which was the same for the model compound **6** (302nm, ε=18,000)$^{6)}$. By using a molar absorptivity of **6**, boron-nitrogen four membered structure in **3c** was detected quantitatively (98% for the expected).



5



6

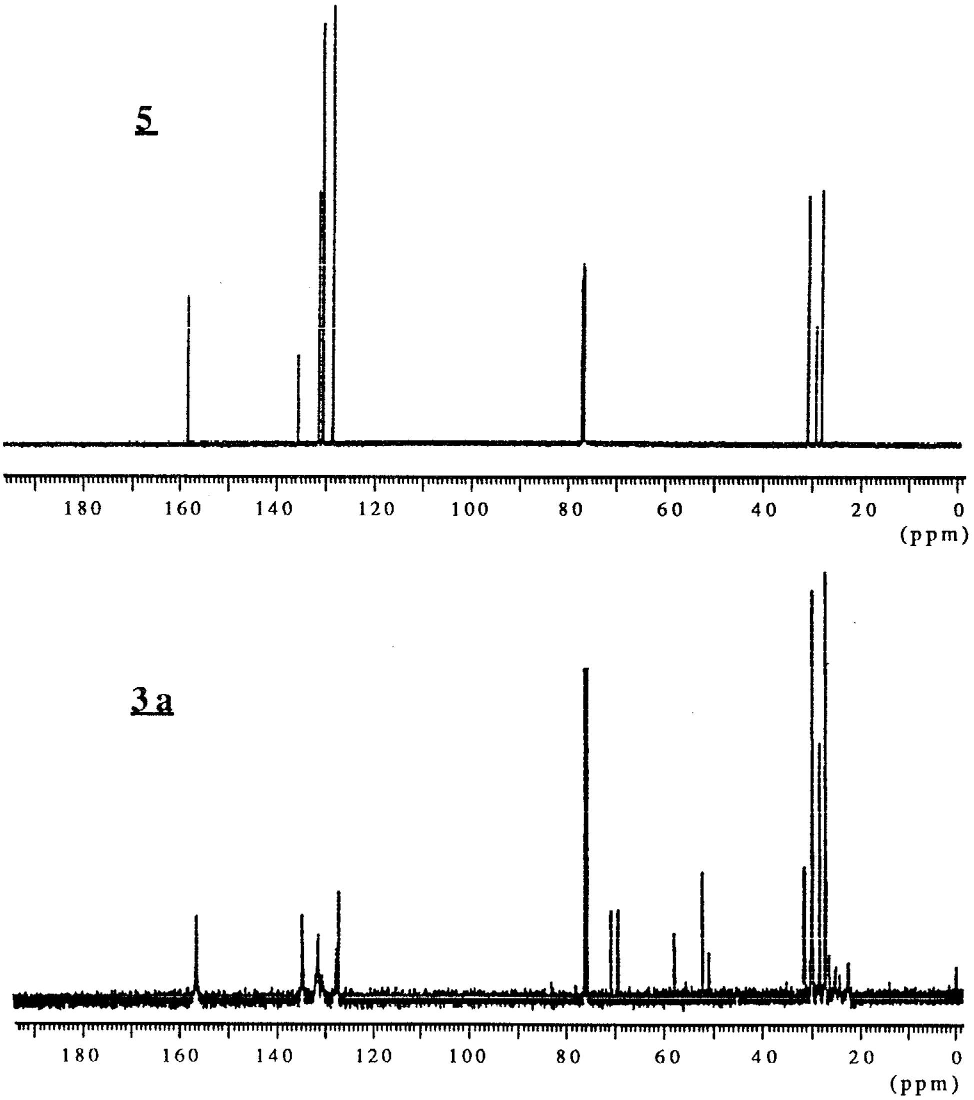
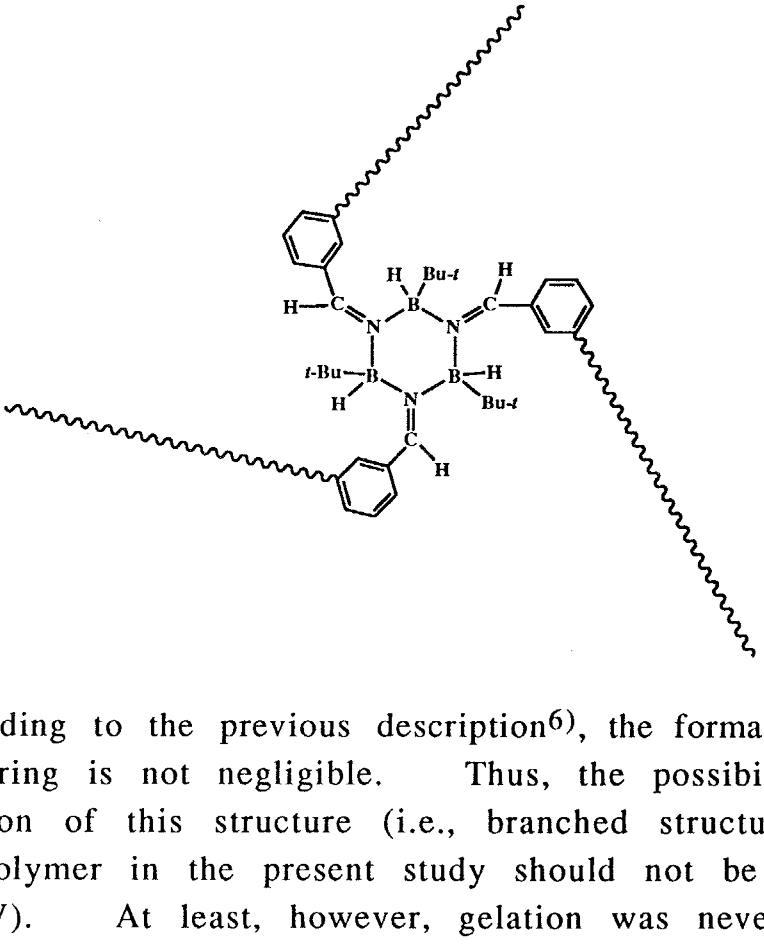


Figure 4 ^{13}C-NMR of 3a and 5.

In their ^{1}H-NMR, as shown in Figure 3, both **3a** and **5** showed peaks assignable to the protons of imine, benzene ring, and *t*-butyl groups. The integral ratios of these peaks for **3a** were in good agreement with the calculated values for the expected structure.

In the ^{13}C-NMR spectrum of **3a**, a peak around 156.6ppm assignable to the iminocarbon was observed, while any peak due to nitrile (120ppm) and amine (46ppm) was not detected (Figure 4). Resonances of *t*-butyl groups in **3a** were quite similar to the corresponding peaks of **5**. The multiplicity of these peaks both in ^{1}H- and ^{13}C-NMR was possibly due to the four possible configurations of four-membered structure (i.e., *cis-syn*, *trans-syn*, *cis-anti*, and *trans-anti* isomeric structures).

Scheme IV



According to the previous description[6)], the formation of six-membered ring is not negligible. Thus, the possibility of the contamination of this structure (i.e., branched structure) in the resulting polymer in the present study should not be eliminated (Scheme IV). At least, however, gelation was never observed during the polymerization at 100°C in the present study.

Stability of 3a against Moisture and Air. The stability of **3a** against air was demonstrated by monitoring the change of molecular weight in the GPC while air was bubbled (120ml/min.)

into a chloroform solution of **3a** for one hour. The stability of **3a** against moisture was similarly checked by stirring the chloroform solution of **3a** with water for two days under nitrogen. In both cases, no obvious change in its molecular weight was observed in comparison with that of the starting polymer (Figure 5). ^{1}H-NMR and IR spectra of the polymer either after air bubbling or after water shaking study were identical to those of the starting polymer.

$\underline{\textbf{3a}}$ (GPC-1)

$$\underline{\textbf{3a}} \xrightarrow[\text{in } CHCl_3]{\text{Shaking with } H_2O} \text{GPC-2}$$

$$\underline{\textbf{3a}} \xrightarrow[\text{in } CHCl_3]{\text{60min. Air bubbling}} \text{GPC-3}$$

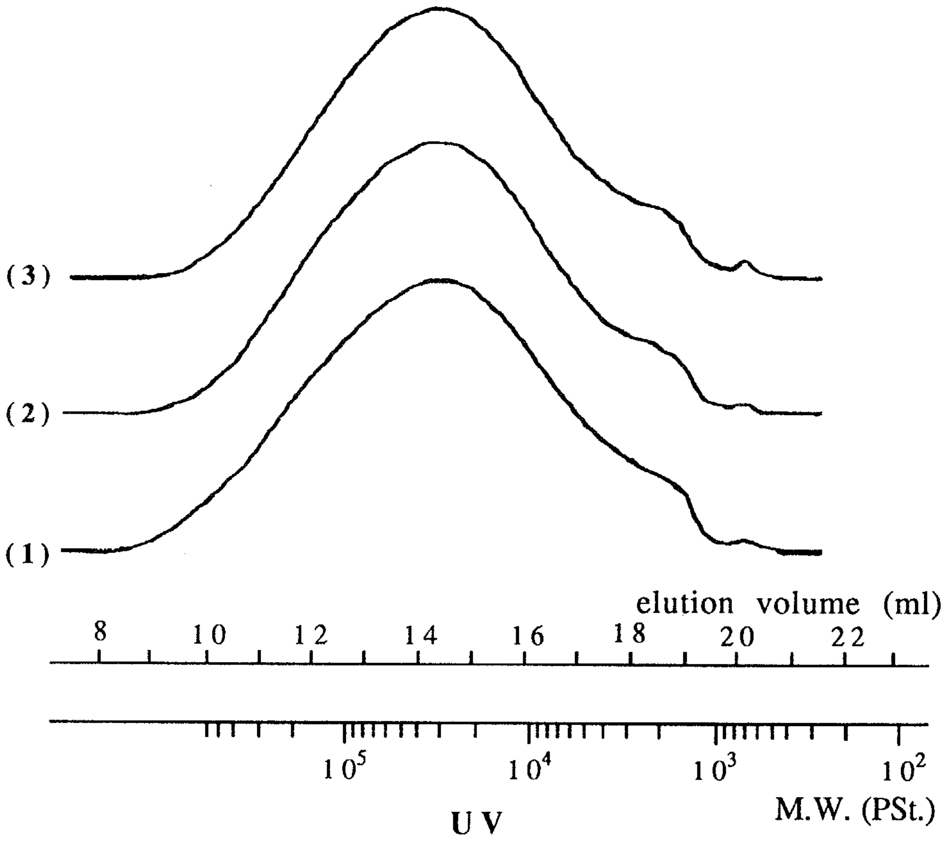


Figure 5 Stability of $\underline{\textbf{3a}}$ against air and moisture.
(1) GPC trace of the starting polymer.
(2) After shaking with water for 2 days.
(3) After air-bubbling for 60 min.

According to Hawthorne6), the iminoborane dimer (**5**) is decomposed into the corresponding benzaldehyde when **5** was refluxed with H_2SO_4/EtOH/H_2O for one day. In the present study, the polymer (**3a**) did not produce isophthalaldehyde under the same reaction conditions. After the reaction, however, in its GPC analysis, the molecular weight of the polymer shifted to a lower molecular weight region. In the IR spectrum of the oligomer obtained showed a peak around 1700cm^{-1}, indicating the presence of aldehyde groups.

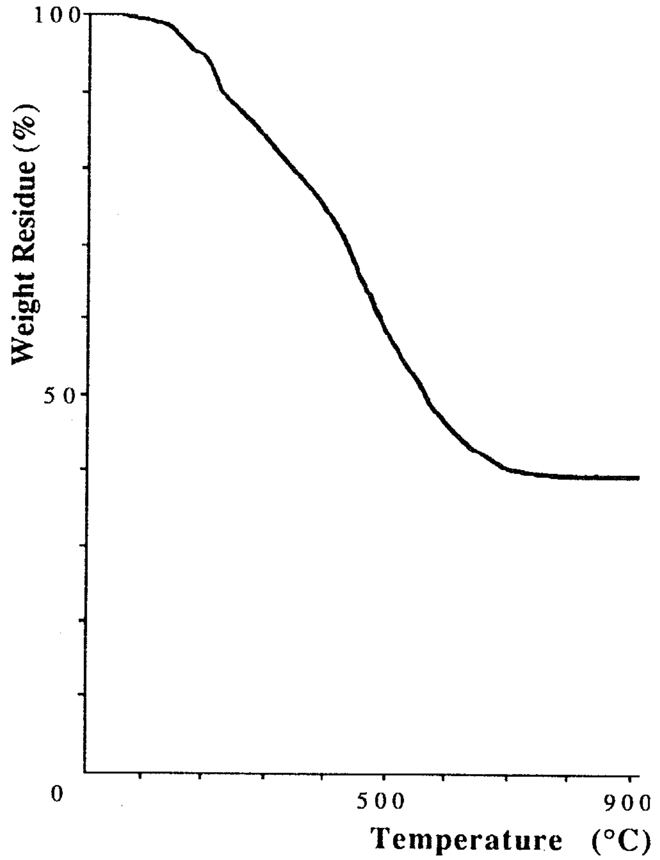


Figure 6 TGA trace of 3a under nitrogen.

TGA analysis of **3a** (Figure 6) shows that the weight loss started at 140°C, and completed at 700°C to form a black solid (40%) under nitrogen flow. DSC was also measured under a nitrogen stream. At 200°C, an irreversible exothermic peak was observed. After the measurement, the polymer became insoluble, and no C=N was observed in its IR spectrum. This may be ascribed to the intermolecular reaction of C=N with B-H groups in the polymer structure.

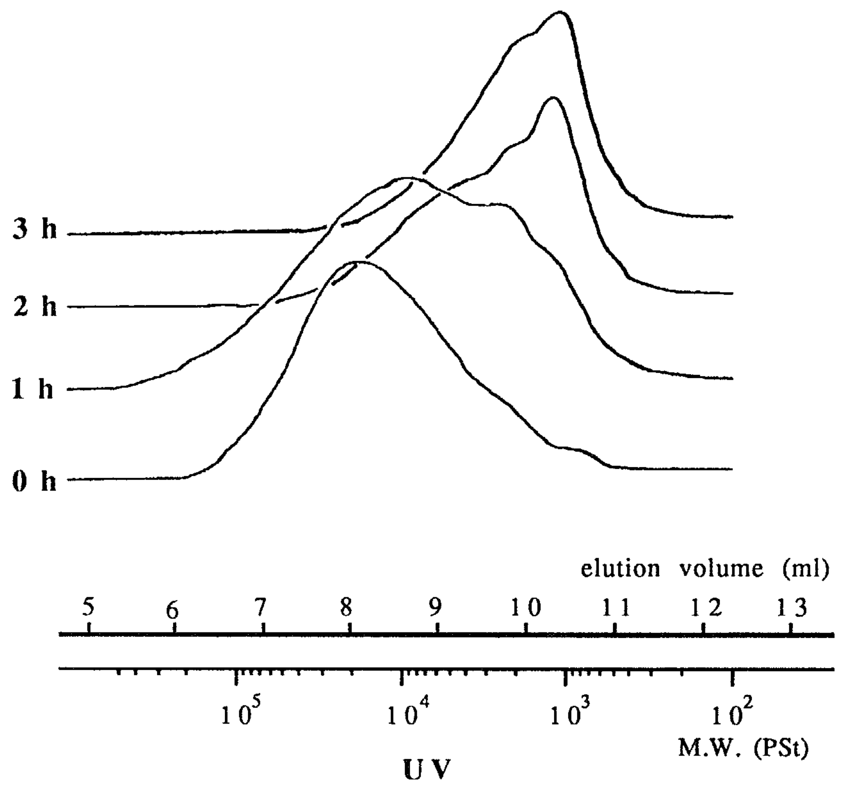


Figure 7 Thermal degradation of 3a at 100°C.

Thermal stability of the polymer in solution was also examined by monitoring the change of molecular weight in the GPC after heating a diglyme solution of **3a** at 100°C under nitrogen (Figure 7). After one hour, the peak became broader, and further heating formed mainly an insoluble material. This result may indicate the formation of some crosslinked materials. The molecular weight of the diglyme-soluble part was lower than that of the starting polymer. The IR spectrum of the obtained insoluble material was, however, identical with that of the starting soluble polymer. There are two possible explanations for crosslinking reaction. One is an intermolecular reaction of C=N with B-H as discussed in the result of DSC, although the concentration of crosslinking reaction was too low to be detected by a spectroscopic method. Another possibility is the variation of a four-membered structure into six-membered one in the polymer chain as was reported for the model compound (**5**) above its melting point6).

Experimental Section

Materials and Instruments. Diglyme and *N,N*-dimethylformamide (DMF) were dried over sodium and calcium hydride, respectively, and distilled before use. 4-Cyanophenol, 1,5-dibromopentane, ethanol, benzene, sodium carbonate, and sulfuric acid were used as received. **1** was prepared as reported earlier[14]), and purified by distillation. **2a** and **2b** were recrystallized from ethyl acetate and methanol, respectively. **2d**-**2f** were purified by distillation under reduced pressure.

^{1}H-NMR spectra were recorded in $CDCl_3$ on a Hitachi R-600 instrument (60MHz, tetramethylsilane as an internal standard). ^{11}B, ^{13}C-NMR spectra were recorded in $CDCl_3$ on a JEOL JNM-JX-400 instrument (BF_3OEt_2, tetramethylsilane, external standard, respectively). IR spectra were obtained on a Perkin Elmer 1600 spectrometer. UV spectra were measured on a Hitachi 200 UV-VIS spectrophotometer. Gas chromatographic analyses were made on a Simadzu GC-6A instrument. Gel permeation chromatographic analyses were carried out on a Tosoh HLC-8020 (TSK gel G3000, G4000, or Shodex AC804) by using THF as an eluent after calibration with standard polystyrene samples. Thermogravimetric analysis (TGA) was made on a Shimadzu DT-30 instrument (15°C/min.) under a nitrogen stream. Differential scanning carolimetry (DSC) was measured on a Seiko DSC200 instrument (10°C/min.).

Synthesis of Monomer (2c). To a 50ml DMF suspension of 4-cyanophenol (2.4g, 20mmol) and sodium carbonate (2.9g, 27mmol) was added 1,5-dibromopentane (2.4g, 10mmol), and the mixture was stirred for 6h at 140°C. The reaction mixture was reprecipitated into 300ml of aqueous sodium hydroxide (1N). The precipitated white solid was filtered and washed with water and then with small amount of ethanol. Yield; 2.5g (86%). Further purification was achieved by the recrystallization from ethyl acetate/*n*-hexane. **2c**; m.p.=112.5-113.5°C; ^{1}H-NMR (δ, ppm) 1.76 ($-CH_2-$, m 6H), 4.03 ($-OCH_2-$, m 4H), 6.77-7.77 (C_6H_4, m 8H); IR (KBr) 2955, 2876, 2221, 1606, 1509, 1471, 1301, 1262, 1173, 1007, 836, 715, 548cm^{-1}.

Synthesis of 3a from 1 and 2a (Table I, run 2). To a 4M diglyme solution of **2a** (0.0579g, 0.452mmol), **1** (0.116g, 0.896mmol, 0.991eq.) was added by using a microfeeder (it took 15 min. to complete the addition) at 100°C under nitrogen. After 1h at that temperature, the reaction mixture was reprecipitated into 20ml of EtOH/H_2O (v/v=1/1). The obtained polymer was freeze-dried with benzene. Yield; 0.116g (96%). All the spectroscopic data of **3a** are given in Results and Discussion. In a similar manner, **3a** was prepared under various conditions. Table I, run 1; from 0.0702g (0.548mmol) of **2a** and 0.144g (1.12mmol, 1.02eq.) of **1** at 80°C. Table I, runs 3 and 4; from 0.241g (1.88mmol) of **2a** and 0.501g (3.95mmol, 1.05eq.) of **1** for 2 and 4.5h, respectively. Table I, run 5; from 0.0926g (0.723mmol) of **2a** and 0.183g (1.42mmol, 0.981eq.) of **1** at 120°C; yield 0.179g (93%). Table II, run 1; from 0.102g (0.795mmol) of **2a** and 0.0648g (0.502mmol, 0.316eq.) of **1**. Table II, run 2; from 0.118g (0.924mmol) of **2a** and 0.116g (0.895mmol, 0.49eq.) of **1**. Table II, run 3; from 0.0642g (0.501mmol) of **2a** and 0.107g (0.825mmol, 0.823eq.) of **1**. Table II, run 5; from 0.0436g (0.340mmol) of **2a** and 0.136g (1.05mmol, 1.55eq.) of **1**; yield 0.0871g (96%). Table II, run 6; from 0.0556g (0.434mmol) of **2a** and 0.243g (1.884mmol, 2.17eq.) of **1**; yield 0.111g (96%). Table II, run 7; from 0.0383g (0.299mmol) of **2a** and 0.229g (1.78mmol, 2.97eq.) of **1**; yield 0.0782g (98%).

Synthesis of 3b-3f from 1 and 2b-2f (Table IV, runs 2-6). Similarly to **3a**, all the boron-containing polymers were prepared as follows. **3b** from 0.0481g (0.375mmol) of **2b** and 0.187g (1.45mmol) of **1**; yield 0.0847g (84%); ^{1}H-NMR (δ, ppm) 0.32-1.21 (CH_3-, 18H), 7.96 (C_6H_4, br, s 4H), 8.41 (N=CH-, br, s 2H); IR (in $CHCl_3$) 2933, 2380, 1642, 1472, 1262, 1207, 1071, 804cm^{-1}. **3c** from 0.0970g (0.335mmol) of **2c** and 0.150g (1.16mmol) of **1**; yield 0.131g (93%); ^{1}H-NMR (δ, ppm) 0.39-1.06 (CH_3-, 18H), 1.78 (-CH_2-, br, m 6H), 4.09 (-OCH_2-, br, m 4H), 6.73-8.06 (C_6H_4, m 8H), 8.26 (N=CH-, br, s 2H); ^{11}B-NMR (δ, ppm) 5.1ppm; IR (in $CHCl_3$) 2953, 2854, 2356, 1641, 1604, 1511, 1469, 1392, 1308, 1255, 1173, 1073, 1032, 959, 910, 834, 734cm^{-1}. **3d** from 0.0498g (0.0461mmol) of **2d** and 0.105g (0.817mmol) of **1**. **3e** from

0.0312g (0.229mmol) of **2e** and 0.0551g (0.427mmol) of **1**. **3f** from 0.435g (2.65mmol) of **2f** and 0.705g (5.46mmol) of **1**.

Stability of 3a under Air. Air was bubbled into 1ml of a chloroform solution of **3a** (0.01g) for 1h (120ml/min.). From the GPC measurement, no decrease of molecular weight was observed. All the spectroscopic data were identical with those for the starting polymer (**3a**). When a boron-containing polymer (**3a**) was kept under air for 1 month in the neat form, no change of molecular weight was observed in GPC measurement.

Stability of 3a in the Presence of Moisture. To a 1ml of chloroform solution of **3a** (0.01g), 1ml of water was added under nitrogen, and the mixture was magnetically stirred for 2 days. From the GPC measurement, no decrease of molecular weight was observed. All the spectroscopic data were identical with those for the starting polymer (**3a**).

Acid Hydrolysis of 3a. To a 1.2ml solution of EtOH/H_2O (v/v=1/3), 0.4 g of conc. sulfuric acid and then 0.2g of **3a** were added. After stirring under reflux for 1 day, the suspension was extracted with diethyl ether, and concentrated. IR spectrum of the product obtained showed a peak around 1700cm^{-1} for aldehyde group. GPC analysis of the product showed lowering of molecular weight (M_n=490, M_w=1,220).

References and Notes

1) See 2-1.
2) See Chapter 3.
3) See 6-1.
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9) (a) Lloyd, J. E.; Wade, K. *J. Chem. Soc.*, **1964**, 1649. (b) Jennings, J. R.; Snaith, R.; Mahmoud, M. M.; Wallwork, S. C.; Brayan, S. J.; Halfpenny, J.; Petch,E. A.; Wade, K. *J. Organomet. Chem.*, **1983**, 249, C1.
10) Weller, F.; Dehnicke, K. *Chem. Ber.*, **1977**, 110, 3935.
11) In its IR, C=N and B-H stretching bands were somewhat weak in comparison with those of the polymer prepared at 100°C as discussed later.
12) M.p.;142.5-144°C (lit.6) 141-143°C).
13) The higher field shift in **3a** may be arisen from the torsion of structure, which is also observed in the UV measurement.
14) Hawthorne, M. F. *J. Am. Chem. Soc.*, **1961**, 83, 831.

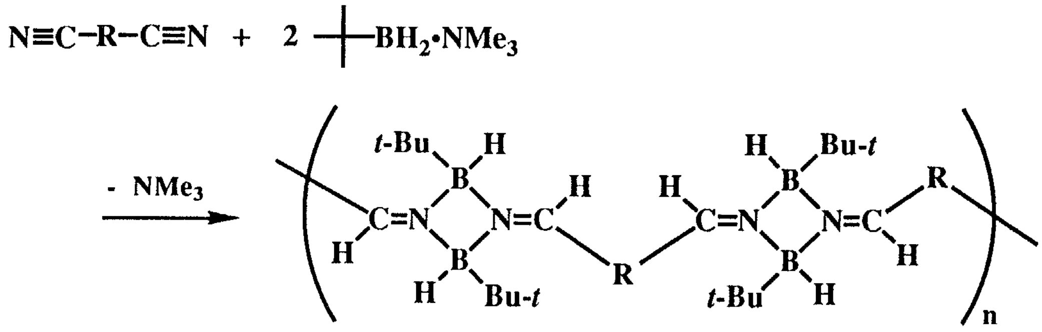
4 - 2

Effect of Alkyl Substituents of Monoalkylboranes on the Hydroboration Polymerization of Dicyano Compounds.

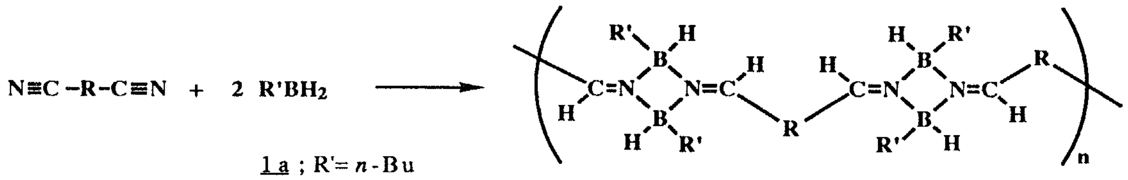
Introduction

In Section 1, the author has described the synthesis of novel boron-containing polymers by the hydroboration polymerization between t-$BuBH_2{\cdot}NMe_3$ and dicyano compounds (Scheme I). The obtained boron-containing polymers were found to be stable enough under air. In this polymerization system, aromatic dicyano monomers such as isophthalonitrile, terephthalonitrile gave polymers having desired structures. Though α,ω-dicyanoalkanes were found to react with t-$BuBH_2{\cdot}NMe_3$, only the corresponding oligomers were obtained due to the further hydroboration reaction of the iminoboranes. These results may indicate that the sufficient reactivity as well as selectivity between hydroboration and dihydroboration (i.e., attacks of B-H towards iminoborane) are required for the synthesis of poly(cyclodiborazane)s. If less sterically hindered monoalkylboranes were used as monomers, the iminoboranes generated in the reaction system might be attacked by another borane to produce dibora-amines which may interrupt polymerization or may cause a gelation. In order to know the limitation of the structure of the monomers for the present system, hydroboration polymerizations of dicyano compounds with less sterically hindered n-$BuBH_2$ and i-$PrBH_2$, as well as more sterically hindered thexylborane were carried out here (Scheme II).

Scheme I



Scheme II



1a ; R'= *n*-Bu
1b ; R'= *i*-Pr
1c ; R'= thexyl

Results and Discussion

Hydroboration Polymerization with *n*-BuBH$_2$•NMe$_3$ or *i*-PrBH$_2$•NMe$_3$. Monoalkylboranes having bulky alkyl substituents could be handled, while those with smaller substituents are usually unstable to be decomposed to the disproportionated products$^{1)}$. On the other hand, monoalkylborane-amine complexes are known to be a good candidate to generate the corresponding free monoalkylboranes *in situ* by the thermal dissociation of amine ligand$^{2)}$. Therefore, monoalkylborane-trimethylamine complexes such as *n*-BuBH$_2$•NMe$_3$ (**1a**), and *i*-PrBH$_2$•NMe$_3$ (**1b**) were examined for the present polymerization.

When two molar equivalent of **1a** (i.e., equimolar amount for the nitrile group) was added to isophthalonitrile (**2**) in diglyme at 100°C, a gelation took place before the complete addition of **1a** (Table I, run 2). A half molar of **1a** gave the soluble oligomer, however, the molecular weight was around a thousand. Under much milder condition (i.e., at 80°C), the reaction took place very slowly, and a part of the reaction mixture became insoluble after the reaction for 4 h.

The model reaction using benzonitrile (**3**) was carried out under various molar ratios of **1a**/**3**, from which the complete conversion of **3** was observed when nearly two fold excess of **1a** was used (Figure 1). These results may indicate that **1a** does not have sufficient selectivity in hydroboration and dihydroboration (i.e., attacks of B-H towards iminoboranes).

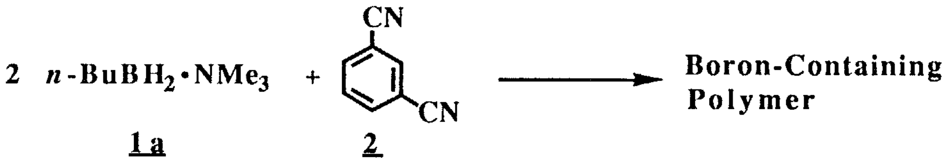


Table I Hydroboration Polymerization of Isophthalonitrile with n-BuBH$_2$·NMe$_3$[a].

Run	$\frac{[n\text{-BuBH}_2]}{[\text{CN}]}$ Ratio	Condition		$\overline{M}_n$[b]	$\overline{M}_w$[b]
1	0.51	100°C	1h	1,150	1,560
2	0.95	100°C	1h	-[c]	-[c]
3	1.67	100°C	1h	-[c]	-[c]
4	1.05	80°C	1h	590	1,120
5			2 h	860	2,910
6			4 h	1,010[d]	15,600[d]

a) Reactions were carried out in diglyme under nitrogen.
b) Estimated by GPC (PSt standard).
c) Gelation was observed during polymerization.
d) Some part of reaction mixture became insoluble in THF.

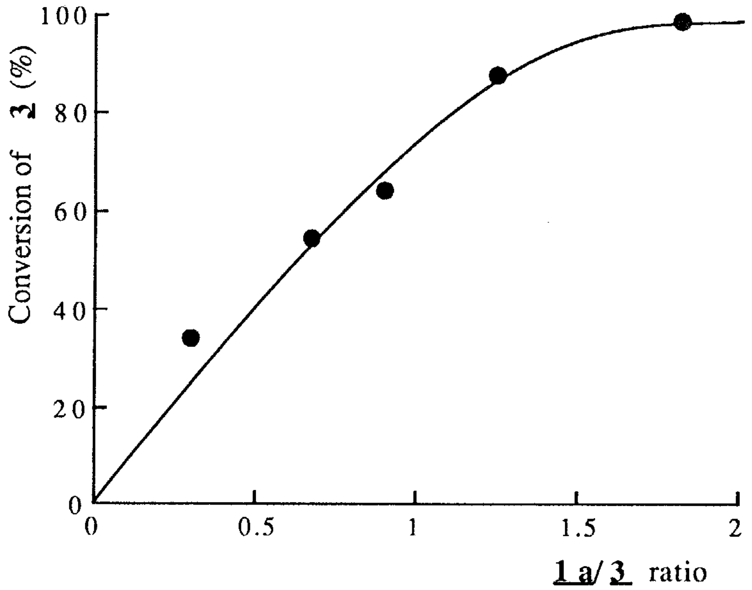
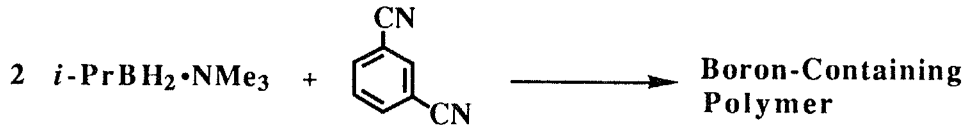


Figure 1 GC conversion curve of 3 by the reaction with 1a.

Similarly, the reaction between **1b** and **2** was carried out in diglyme. Sufficient reactivity was not obtained at 80°C, and a gelation took place at 120°C. However, no gelation was observed in every feeding ratio of two monomers, when reactions were carried out at 100°C (Table II, runs 1-5). The molecular weight of the resulting polymer became higher as the feed ratio of **1b/2** was increased. In the ^{1}H-NMR spectrum of the obtained polymer (run 5), broad peaks at 3.6 and 4.9ppm attributable to the methylene adjacent to the amino-group and bora-amino-group, respectively, were observed$^{3)}$. While the polymerization between **1b** and **2** gave a soluble polymer under the examined reaction condition, the structure of the obtained polymer was found to contain primary amines by the attack of B-H towards iminoborane species.



1b 2

Table II Hydroboration Polymerization of Isophthalonitrile with i-PrBH$_2$•NMe$_3$ $^{a)}$.

Run	$\frac{[i\text{-PrBH}_2]}{[\text{CN}]}$ Ratio	Condition		$\overline{M}_n$ $^{b)}$	$\overline{M}_w$ $^{b)}$
1	0.54	100°C	1h	630	1,030
2	0.71	100°C	1h	870	2,410
3	1.10	100°C	1h	950	2,450
4	1.50	100°C	1h	2,430	19,000
5	2.14	100°C	1h	3,040	20,300
6	1.06	80°C	1h	490	650
7			2 h	590	960
8			3 h	740	1,500
9	1.07	120°C	1h	gelation	

a) Reactions were carried out in diglyme under nitrogen.
b) Estimated by GPC (PSt standard).

When the model reaction of **1b** with **3** was carried out under various feed ratios of **1b**/**3**, the conversion of **3** was found to become closer to the theoretical 1:1 reaction in comparison with that of the reaction with **1a** (Figure 2). However, the complete conversion of **3** was not observed when an equimolar amount of **1b** was used for the reaction, which is rather different from the result using *t*-BuBH$_2$•NMe$_3$.

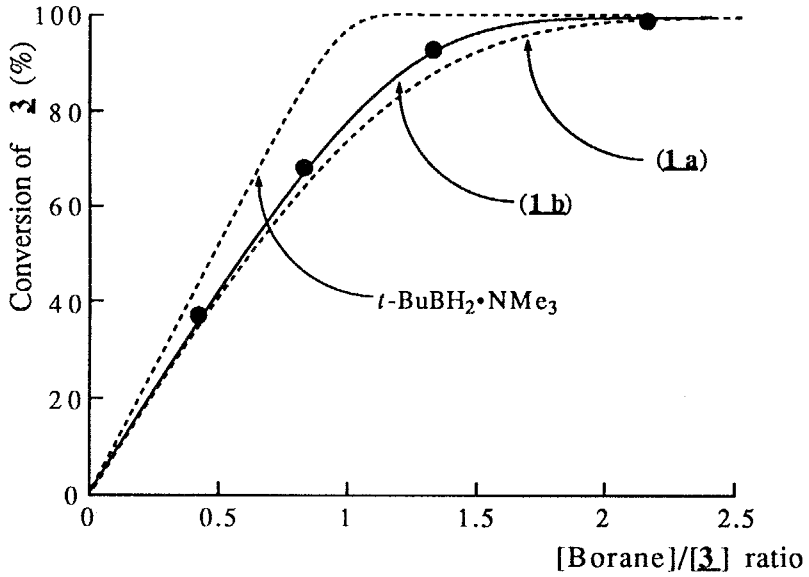
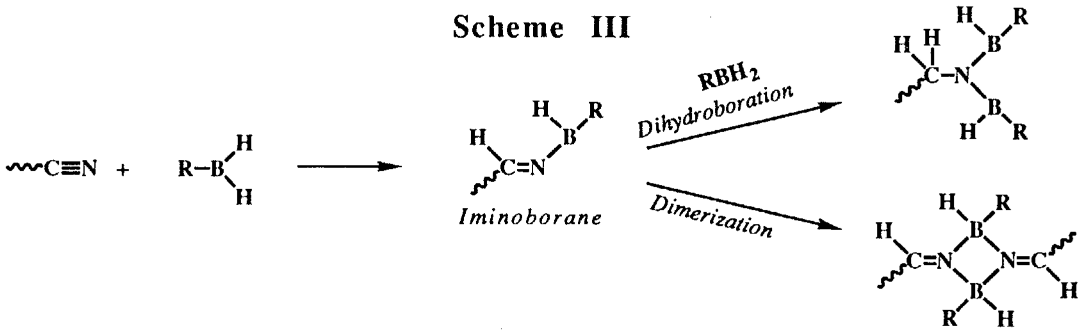


Figure 2 **GC conversion curve of 3 by the reaction with 1b.**

From the results obtained from the reactions of **1a**, **1b**, and *t*-BuBH$_2$•NMe$_3$[4], hindered alkyl groups seem to play an important role to prevent the further hydroboration reaction of iminoborane species, as shown in Scheme III.

Scheme III



Hydroboration Polymerization with Thexylborane. Hydroboration reaction of **2** with thexylborane was very slow, and no polymer was obtained under similar conditions. However, hydroboration reaction of cyanoalkanes with **1c** was found to proceed smoothly when the reaction was carried out at ambient temperature without any solvent. In the case of adiponitrile (**4a**), the reaction with **1c** produced a colorless gum within 1 h at room temperature which was soluble in organic solvents. By the reprecipitation with ethanol/water (v/v=1/3), the oligomer (**5ca**) was obtained in 54% yield. The structure of **5ca** was elucidated by ^{11}B-, ^{1}H-NMR, and IR spectra. In its ^{11}B-NMR spectrum, two peaks at 33.7 and 3.2ppm were observed (Figure 3). The former peak can be attributed to the three coordinated boron species (i.e., monomeric iminoborane and/or dibora-amine), and the latter to the dimeric iminoborane.

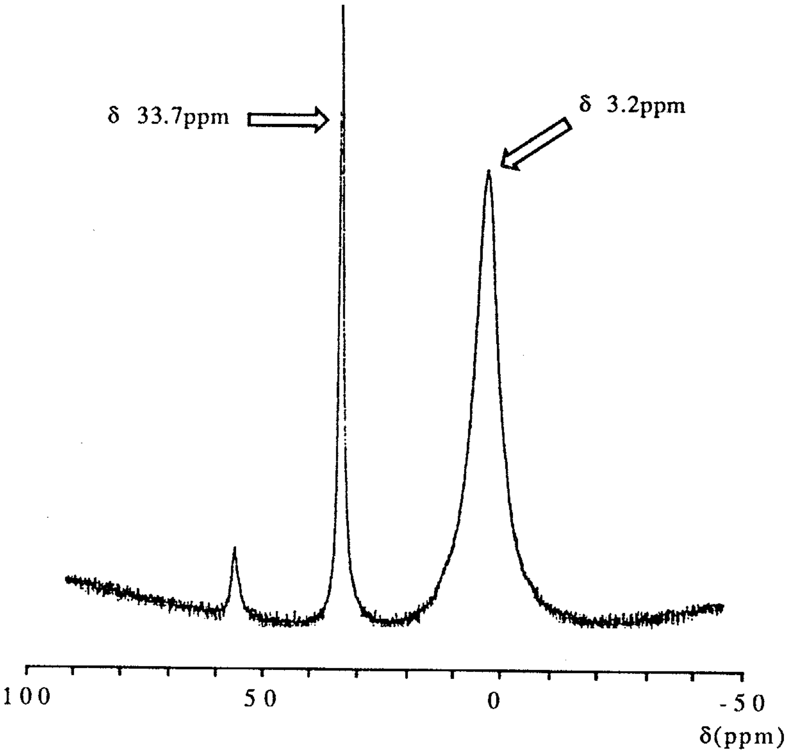


Figure 3 ^{11}B-NMR spectrum of 5ca.

In its ^{1}H-NMR, methyl groups of thexyl, inner methylenes, methylenes adjacent to iminoborane, and protons of imines were observed (Figure 4). The intensity of the peak for the protons of the imine was smaller than expected in comparison with other peaks, and a small peak at 3.3ppm attributable to the methylenes adjacent to bora-amino group was observed.

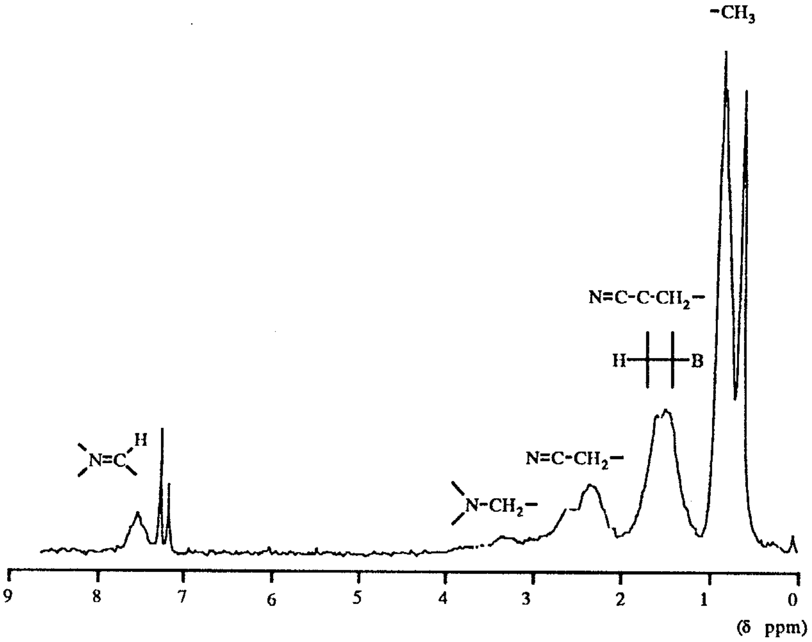


Figure 4 ^{1}H-NMR spectrum of 5ca.

In the IR spectrum, specific peaks at 2,371 (υ_{B-H}) and 1,673 cm^{-1} ($\upsilon_{C=N}$) were observed (Figure 5). No peaks attributable to nitrile, nor monomeric iminoborane5) were detected. Therefore, it can be concluded that the structure of the polymer contains the expected cyclodiborazane backbones. The lower molecular weight of the polymer could be explained not by the insufficient dimerization, but by the side reaction (i.e., further hydroboration reaction of iminoboranes to the dibora-amines).

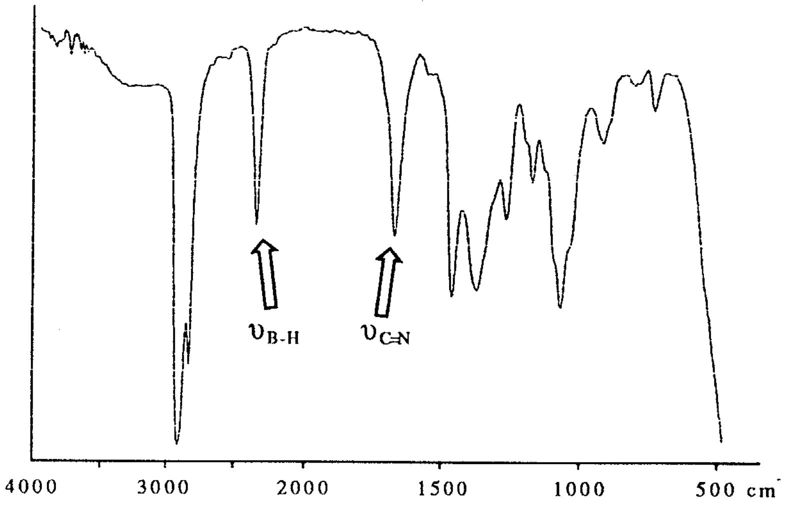


Figure 5 IR spectrum of 5ca.

Similarly, polymerization between **1c** and several dicyanoalkanes (**4b**-**4d**) were examined (Table III). In all cases, reactions were carried out in bulk, and the reaction mixture became viscous within 1 h. Whole of the oligomers thus obtained (**5cb**-**5cd**) were confirmed to have cyclodiborazane backbone from the results of spectroscopic measurements. Though **1c** has too sterically hindered alkyl substituents on the boron atom to attack the aromatic cyano groups, the higher steric hindrance in **1c** in comparison with *t*-$BuBH_2{\bullet}NMe_3$ made it possible to produce the oligomers from α,ω-dicyanoalkanes which are difficult monomers to be polymerized with *t*-$BuBH_2{\bullet}NMe_3$ due to the dihydroboration.

Table III Hydroboration Polymerization of Various Dicyano Compounds with Thexylborane[a].

Run	Dicyano Compounds	Yield (%)[b]	$\overline{M}_n$[c]	$\overline{M}_w$[c]
1	$NC(CH_2)_4CN$ (4a)	54	1,250	3,680
2	$NC(CH_2)_5CN$ (4b)	48	1,030	3,520
3	$NC(CH_2)_6CN$ (4c)	63	740	1,660
4	$NC(CH_2)_8CN$ (4d)	58	660	1,460

a) Reactions were carried out in bulk under N_2.
b) Isolated yields after reprecipitation into $EtOH/H_2O$ (v/v=1/3).
c) Estimated by GPC (PSt standard).

Similarly to the polymers from *t*-$BuBH_2{\bullet}NMe_3$ and dicyano monomers, the oligomers thus obtained were quite stable to handle under air. From the thermogravimetric analysis of **5c** under nitrogen, 12% of the residue remained after the heating up to 900°C (Figure 6). This result indicates that the boron-containing oligomers obtained here might be utilized as precursors for the boron-containing inorganic materials.

The study presented in this section has shown the limitation of alkyl substituents of monoalkylborane monomers on the hydroboration polymerization of dicyano compounds, which may give a useful information to design poly(cyclodiborazane)s from various monoalkylboranes and dicyano compounds.

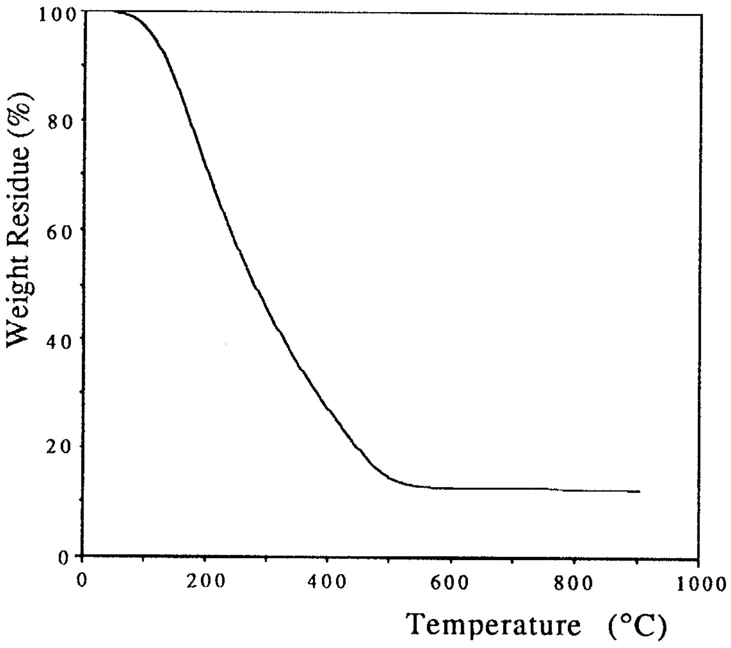


Figure 6 TGA of 5ca under nitrogen.

Experimental Section

Materials and Instruments. **1a** and **1b** were obtained by the reaction of the corresponding trialkylboroxines[6)] with lithium aluminum hydride in the presence of trimethylamine as previously described, and were purified by distillation[2)]. **1c** was obtained by the reaction between borane-dimethyl sulfide and 2,3-dimethyl-2-butene, as reported earlier[7)], and was purified by distillation[8)]. **2** was purified by recrystallization from ethyl acetate. **3** and α,ω-dicyanoalkanes were purified by distillation under reduced pressure.

^{1}H-NMR spectra were recorded in $CDCl_3$ on a Hitachi R-600 instrument (60MHz, tetramethylsilane as an internal standard). IR spectra were obtained on a Perkin Elmer 1600 spectrometer. ^{11}B-NMR spectrum was recorded in $CDCl_3$ on a JEOL JNM-JX-400 instrument (128MHz, BF_3OEt_2 as an external standard). Gas chromatographic analyses were made on a Simadzu GC-6A instrument. Gel permeation chromatographic analyses were carried out on a Tosoh HLC-8020 (TSK gel G3000) after calibration with standard polystyrene samples. Thermogravimetric analysis

(TGA) was made on a Shimadzu DT-30 instrument (15°C/min.) under nitrogen stream.

Polymerization Reaction of 1a and 2. A typical procedure is shown as follows (Table I, run 1): In a two-way reaction flask equipped with a stirrer tip, a septum inlet, and a reflux condenser with a three-way cock, **2** (0.0623g, 0.486mmol) and diglyme (0.12ml) was introduced under nitrogen. To this solution, **1a** (0.0635g, 0.492mmol) was added using a microfeeder at 100°C. The reaction mixture was kept stirring for additional 1h at that temperature. Diglyme was removed under vacuum and the obtained product was subjected to the GPC measurement. Similarly, other experiments in Table I (runs 2-6) were carried out using the following monomer feedings: **2** (0.0611g, 0.477mmol) and **1a** (0.117g, 0.904mmol, run 2), **2** (0.0631g, 0.492mmol) and **1a** (0.210g, 1.63mmol, run 3), and **2** (0.0562g, 0.439mmol) and **1a** (0.119g, 0.920mmol, runs 4-6), respectively.

Model Reaction of 1a with 3. To a nitrogen-replaced two-way flask containing **3** (0.0873g, 0.847mmol), tetradecane (0.040g, as an internal standard), and diglyme (0.2ml), was added **1a** (0.0327g, 0.253mmol, 29.9 mol% of **3**) by using a microfeeder (it required 10 min. for the complete addition) at 100°C. After the reaction for 1h at 100°C, the conversion of **3** was measured by GC (conversion; 34.4%). Similarly, a series of the experiments were carried out by using the different molar ratios as follows: **3** (0.158g, 1.53mmol) and **1a** (0.133g, 1.03mmol, **1a**/**3**=0.674), **3** (0.0947g, 0.918mmol) and **1a** (0.107g, 0.827mmol, **1a**/**3**=0.901), **3** (0.0742g, 0.720mmol) and **1a** (0.117g, 0.903mmol, **1a**/**3**=1.25), and **3** (0.0874g, 0.848mmol) and **1a** (0.199g, 1.54mmol, **1a**/**3**=1.82), respectively.

Polymerization Reaction of 1b and 2. A typical procedure is shown as follows (Table II, run 1): In a two-way reaction flask equipped with a stirrer tip, a septum inlet, and a reflux condenser with a three-way cock, **2** (0.0450g, 0.327mmol) and diglyme (0.13ml) were introduced under nitrogen. To this solution, **1b** (0.0620g, 0.539mmol) was added using a microfeeder at 100°C. The reaction mixture was kept stirring for additional 1h at that temperature. Diglyme was removed under vacuum and the obtained product was subjected to the GPC measurement. Similarly, other experiments in Table I (runs 2-9) were carried out using the following monomer feedings: **2** (0.0509g, 0.397mmol) and **1b** (0.0649g, 0.564mmol, run 2), **2** (0.0438g, 0.342mmol) and **1b** (0.0868g, 0.755mmol, run 3), **2** (0.0419g, 0.327mmol) and **1b** (0.113g, 0.980mmol, run 4), **2** (0.0454g, 0.354mmol) and **1b** (0.175g, 1.52mmol, run 5), **2** (0.0612g, 0.478mmol) and **1b** (0.116g, 1.01mmol, runs 6-8), and **2** (0.0419g, 0.327mmol) and **1b** (0.0805g, 0.700mmol, run 9), respectively. Typical spectroscopic data of the polymer (in Table II, run 5) are shown as follows; ^{1}H-NMR (δ, ppm) 0.36-1.98 (i-C_3H_7, m), 3.6 ($-CH_2-N$, br, m), 4.9 ($-CH_2-N-B$, br, m), 7.1-8.6 (C_6H_4, $-CH=N$, m), (integral ratios; 2.7:0.16:0.13:1); IR (in $CHCl_3$) 2941, 2860, 2358, 1651, 1462, 1097, 1034cm^{-1}.

Model Reaction of 1b with 3. Similarly to the case of model reaction of **1a** with **3**, a series of the experiments were carried out by using the different molar ratios of **1b/3** as follows: **3** (0.108g, 1.04mmol) and **1b** (0.050g, 0.438mmol, **1b/3**=0.421), **3** (0.0914g, 0.886mmol) and **1b** (0.0847g, 0.736mmol, **1b/3**=0.831), **3** (0.0766g, 0.743mmol) and **1b** (0.114g, 0.989mmol, **1b/3**=1.33), and **3** (0.0687g, 0.666mmol) and **1b** (0.166g, 1.44mmol, **1b/3**=2.16), respectively.

Polymerization Reaction of 1c with α,ω-Dicyanoalkanes (4a-4d). A typical procedure is shown as follows (Table III, run 1): To a nitrogen-replaced flask equipped with a stirrer tip and a three-way cock, **4a** (0.0657g, 0.608mmol) and then **1c** (0.114g, 1.16mmol, 0.96 eq. for nitrile) were added at ambient temperature. In the early stage of the reaction, the reaction proceeded in two phase system which turned to an uniphase system as the reaction product became viscous (it took less than 30 min.). After the reaction for 1h, the viscous reaction mixture was dissolved in THF and was precipitated into ethanol/water (v/v=1/3). After freeze-drying with benzene, **5ca** was obtained as a colorless gum (0.100g, 54% yield). Spectral data are shown in Results and Discussion.

Similarly, other boron-containing oligomers in Table III, runs 2-4, were prepared from the corresponding dicyano monomers and **1c**. **5cb** (from **4b** (0.0685g, 0.561mmol) and **1c** (0.114g, 1.16mmol)): 48% yield (0.086g); ^{1}H-NMR (δ, ppm) 0.20-0.98 (-CH_3, m), 1.02-1.93 (CH, -CH_2-C-C=N, m), 1.93-2.78 (-CH_2-C=N, m), 3.28 (-CH_2-N, m), 7.59 (-CH=N, br, m), (integral ratios; 9.2:6.6:2.7:0.78:1); IR (neat) 2934, 2864, 2375, 1673, 1463, 1372, 1066, 932cm^{-1}.

5cc (from **4c** (0.0705g, 0.518mmol) and **1c** (0.108g, 1.10mmol)): 63% yield (0.108g); ^{1}H-NMR (δ, ppm) 0.22-1.05 (-CH_3, m), 1.08-2.00 (CH, -CH_2-C-C=N, m), 2.00-2.99 (-CH_2-C=N, m), 3.32 (-CH_2-N, m), 7.63 (-CH=N, br, m), (integral ratios; 16.9:14:6.1:2.1:1); IR (neat) 3316, 2930, 2862, 2371, 1672, 1465, 1403, 1266, 1065, 894, 759cm^{-1}.

5cd (from **4d** (0.0760g, 0.463mmol) and **1c** (0.103g, 1.05mmol)): 58% yield (0.097g); ^{1}H-NMR (δ, ppm) 0.37-1.04 (-CH_3, m), 1.07-1.90 (CH, -CH_2-C-C=N, m), 1.90-2.82 (-CH_2-C=N, m), 3.32 (-CH_2-N, m), 7.63 (-CH=N, br, m), (integral ratios; 15.4:17.4:5.9:1.8:1); IR (neat) 3206, 2928, 2859, 2370, 1672, 1464, 1371, 1065, 927, 757cm^{-1}.

References and Notes

1) Pelter, A.; Smith, K.; Brown, H. C. In *Borane Reagents*; Academic Press: London, 1988, p178.
2) Hawthorne, M. F. *J. Am. Chem. Soc.*, **1961**, 83, 831.
3) ^{1}H-NMR spectrum was measured after the precipitation with EtOH/H_2O (v/v=1/1). The yield of the obtained product was 139% based on the ideal polymer structure, and the peak for *i*-propyl group was larger than expected. Thus, the structure of the polymer should be contaminated with dibora-amines as well as free amines.
4) See 4-1.
5) Monomeric iminoboranes are known to have their C=N vibration spectra around 1,800cm^{-1}. See, for example, (a) Mikhailov, B. M.; Ter-Sarkisyan, G. S.; Govorov, N. N.; Nikolaeva, N. A. *Izv. Akad. Nauk SSSR, Ser. Khim.*, **1976**, 1820. (b) Mikhailov, B. M.; Ter-Sarkisyan, G. S.; Govorov, N. N. *ibid.*, **1976**, 1823.
6) McCusker, P. A.; Ashby, E. C.; Makowski, H. S. *J. Am. Chem. Soc.*, **1957**, 79, 5179.

7) Brown, H. C.; Mandal, A. K.; Kulkarni, S. U. *J. Org. Chem.*, **1977**, 42, 1392.
8) See 2-1.

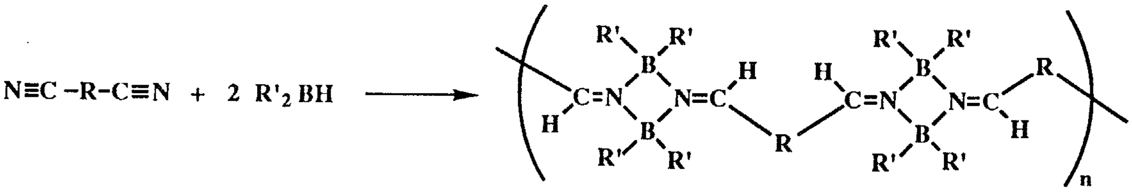
4 - 3

Synthesis of Boron-Containing Polymers by the Reaction between Dialkylborane and Dicyano Compounds.

Introduction

In Se4ctions 1 and 2, the author has described a novel synthetic methodology to obtain boron-containing polymers by hydroboration reactions of dicyano monomers with monoalkylborane derivatives. By using this method, polymers having derivatives of cyclodiborazane backbones were produced. The boron atoms in the polymer are, however, always attached to one alkyl group and a hydride. Because of the interests in polymerization behavior, as well as to extend the possibilities to obtain boron-containing materials, hydroboration polymerization of dicyano compounds with dialkylboranes were examined here (Scheme I). Since the polymers obtained here should have no boron-hydride moieties in the structure of the polymer, the stability of the polymer might be expected to be better than or as well as those from monoalkylboranes.

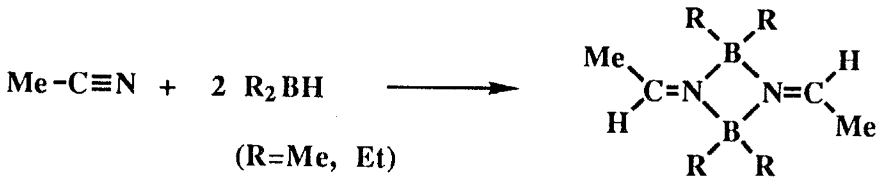
Scheme I



Results and Discussion

According to the previous report by Lloyd and Wade1), the reaction of dimethylborane or diethylborane (existing as their dimers) with nitriles such as acetonitrile gives the corresponding dimers of iminoboranes (i.e., derivatives of cyclodiborazanes, Scheme II). In this system, boron atoms in the cyclodiborazane contain two alkyl groups and the products were known to be stable under air. If dialkylboranes were used for the polymerization with dicyano monomers, the boron-containing polymers having corresponding structures might be produced.

Scheme II



For the dialkylborane monomer, di-*n*-butylborane (**1**, exists as its dimer) was used here, and the polymerization with adiponitrile (**2c**) was examined at ambient temperature. Among the examined reaction media (e.g., dichloromethane, THF, and without any solvents), the reaction in bulk gave the best result. Although the reaction initially proceeded by a two-phase system, a viscous gum was obtained within one hour2). Therefore, the following studies were examined in bulk conditions. As summarized in Table I, polymerization reactions were carried out by changing the feed ratio of two monomers from 0.65 to 2.16 on the basis of [B-H]/[C≡N].

While the isolated yields of the polymers (**3c**) (runs 1-4; based on **1**, runs 5-8; based on **2c**) were always around 80-90%, the molecular weights of **3c** were largely decreased in the presence of a large excess amount of **1**. The present hydroboration polymerization can be classified as a step-growth polymerization, the molecular weights of the polymers should be effected by the feed ratio of two monomers. However, in the present system, only the excess borane influenced on the molecular weight of the resulting polymer. Although there are no evidences to support an idea to explain these phenomena, the observed insensitivity on the feed ratio might be rationally explained if the reaction is supposed to proceed in the borane phase. In the case that an excess amount of **2c** is used for the polymerization, only a small part of **2c** gradually dissolves into borane phase which participates in polymerization. Thus, excess amount of **2c** remained unreacted in another phase. On the other hand, in the presence of excess amount of **1**, the unreacted **1** always exists in the polymerization system, which interrupts polymerization by some side reactions such as second hydroboration towards iminoboranes.

Table I Hydroboration Polymerization of Adiponitrile with Dibutylborane under Varied Feed Ratios.[a)]

Run	$\frac{[B-H]}{[C\equiv N]}$ ratio	Yield[b)] (%)	$\overline{M}_n$[c)]	$\overline{M}_w$[c)]
1	0.65	91	18,700	46,400
2	0.76	82	22,700	56,400
3	0.83	85	19,100	53,600
4	0.90	78	17,100	51,700
5	1.02	82	16,900	53,700
6	1.10	83	16,100	57,200
7	1.42	79	9,930	29,400
8	2.16	79	910	1,590

a) Polymerizations were carried out in bulk at r.t.
b) Isolated yields after precipitation into EtOH/H_2O (v/v=1/1).
Runs 1-4; based on 1, Runs 5-8; based on 2c.
c) GPC (THF), polystyrene standard.

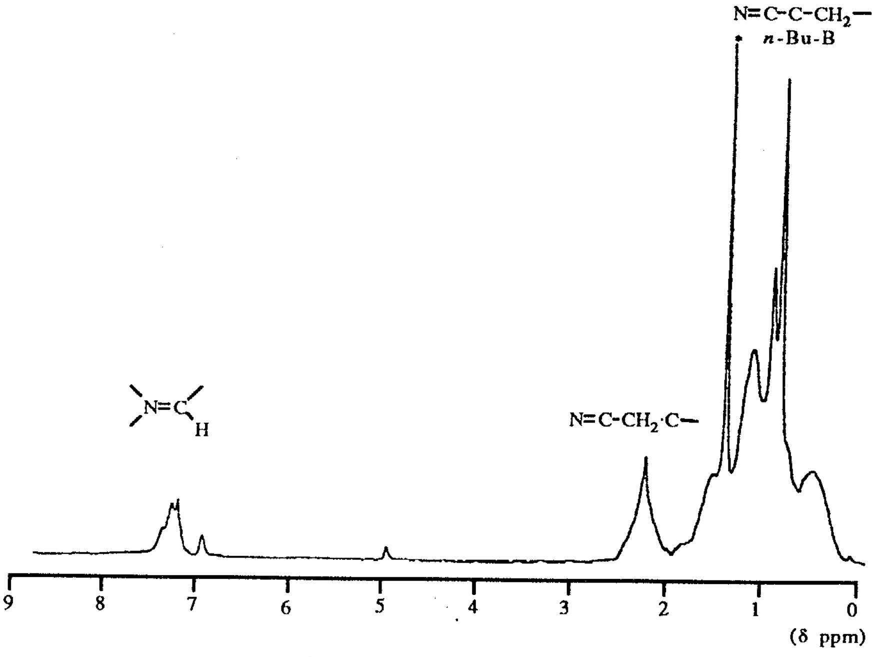


Figure 1 ^{1}H-NMR spectrum of 3c.

The structure of the obtained polymer (3c) was confirmed by ^{11}B-, ^{1}H-NMR, and IR spectra. In the ^{1}H-NMR spectrum, protons of imines, methylenes adjacent to imines, and other protons (inner methylenes and *n*-butyl group on the boron atom) were observed

(Figure 1). The integral ratios of these peaks were in good agreement with the expected structure. In the ^{11}B-NMR, a broad peak at 5.5ppm attributable to the four coordinated boron species (i.e., iminoborane dimers) was observed (Figure 2). In its IR spectrum, an absorption at 1,684cm^{-1} which can be attributed to the iminoborane dimers was observed (Figure 3). The peaks for boron-hydride or nitrile were not detected. These results show that **3c** does not contain the undesirable structures such as dibora-amines as a result of dihydroboration.

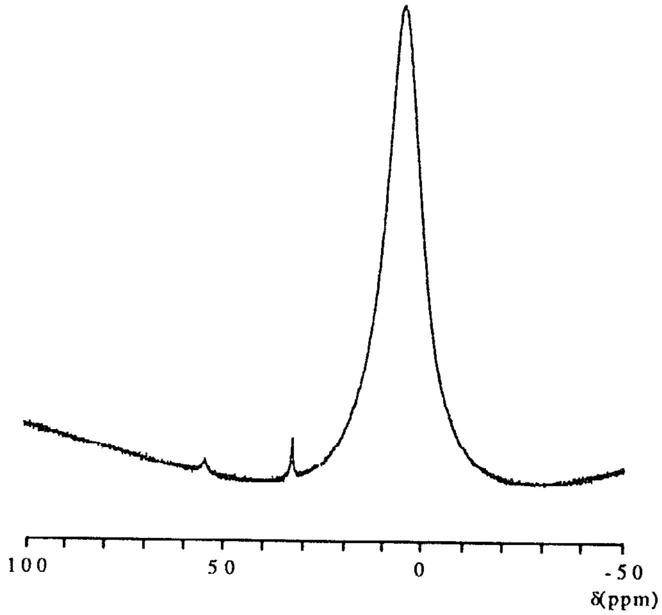


Figure 2 ^{11}B-NMR spectrum of 3c.

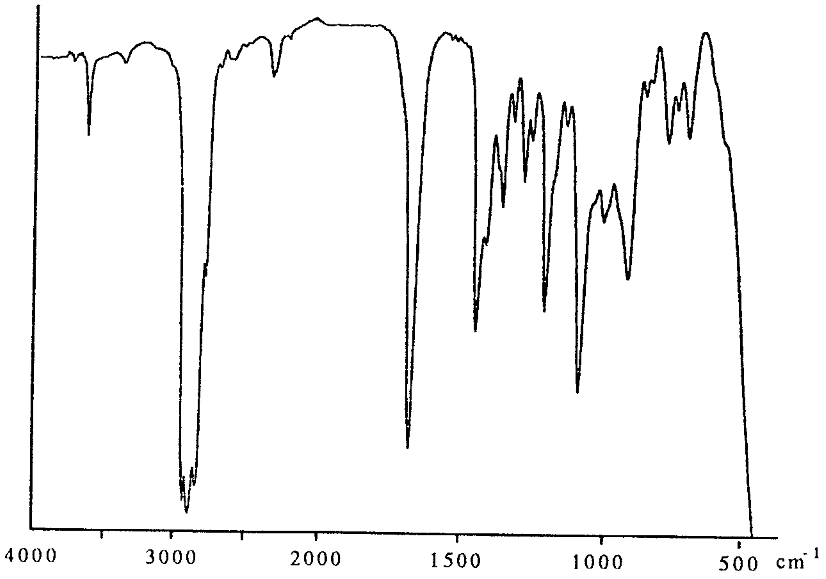


Figure 3 IR spectrum of 3c.

Table II summarizes the results of polymerizations of **1** with various dicyano compounds (**2a**-**2g**). In the case of aliphatic dicyano monomers, the corresponding polymers were obtained in high yields. Monomers having longer methylene chains (**2e** and **2f**) produced lower molecular weight polymers in comparison with those having shorter methylenes (**2a**-**2d**) (runs 5, 6 vs. runs 1-4). In the case of **2e** and **2f**, two monomers dissolved each other to produce homogeneous system just after the addition of two monomers. These differences should be due to the low polarity in the case of **2e** and **2f**, different from much polar **2a**-**2d**. Although the results clearly indicated that compatibility of two monomers had a large effect on the molecular weight of the resulting polymers, it is not clear about the reason why the two-phase system is suitable to make polymers having higher molecular weights. In the case of solid dicyano monomers (**2a** and **2g**), the yields of the resulting polymers were rather low, presumably because polymerizations may proceed to produce viscous gum before the complete reaction of dicyano monomers. Accordingly, polymerization of **2a** was carried out above its melting point (70°C) at the early stage of the reaction to give the polymer **3a** in high yield (run 1).

Table II Hydroboration Polymerization of Various Dicyano Compounds with Dibutylborane.[a)]

Run	Dicyano Compounds	Yield[b)] (%)	$\overline{M}_n$[c)]	$\overline{M}_w$[c)]
1[d)]	$NC(CH_2)_2CN$ (2a)	88	16,800	49,900
2	$NC(CH_2)_3CN$ (2b)	90	10,100	23,500
3	$NC(CH_2)_4CN$ (2c)	78	17,100	51,700
4	$NC(CH_2)_5CN$ (2d)	77	25,000	69,900
5	$NC(CH_2)_6CN$ (2e)	76	3,080	5,830
6	$NC(CH_2)_8CN$ (2f)	88	5,930	9,070
7	m-$NC-C_6H_4-CN$ (2g)	25	3,540	14,700

a) Polymerizations were carried out in bulk at r.t.

b) Isolated yields after precipitation into $EtOH/H_2O$ (1/1).

c) GPC (THF), polystyrene standard.

d) Polymerization was carried out at 70°C for 30min., then at r.t. for 2h.

The air-stability of **3c** was demonstrated by checking the change of its molecular weight in GPC after keeping **3c** under air for a designated period. The molecular weight and the molecular weight distribution of the sample after keeping for 80 days under air were the same in comparison with those of the sample just after polymerization (Figure 4). IR and ^{1}H-NMR spectra of the sample after the storage were identical with those of the sample just after the preparation. Therefore, this boron-containing polymer was concluded to be stable under air.

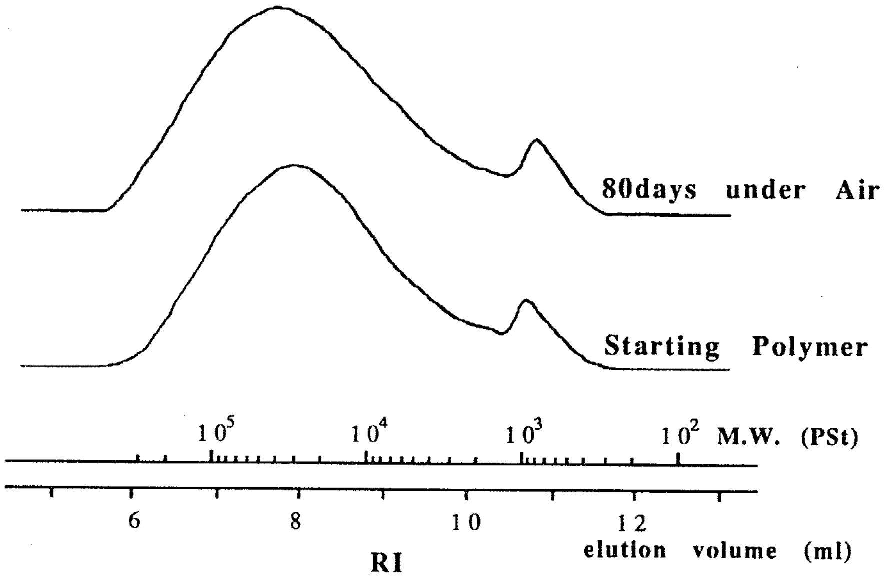


Figure 4 GPC traces for 3c (just after the preparation) and the sample after keeping under air for 80 days.

Thermogravimetric analysis of **3c** was carried out under nitrogen to demonstrate the possibility as a precursor providing inorganic boron-containing materials. As shown in Figure 5, the weight loss started around 140°C, and was completed around 700°C. After the measurement of TGA, about 12% of a residue remained as a black solid. In the DSC measurement, no specific peaks were detected below 140°C.

The molecular weight of the sample after the heating at 140°C, or at 200°C was somewhat decreased as shown in Figure 6. However, they were still soluble in organic solvents, which is completely different from the case of the polymer prepared from monoalkylborane[3]. This better thermal stability might be due to the absence of boron-hydride moiety in the polymer chain prepared from dialkylboranes. That is, polymers from dialkylborane do not have any reactive groups on the boron atom which improved the thermal stability of the boron-containing polymers.

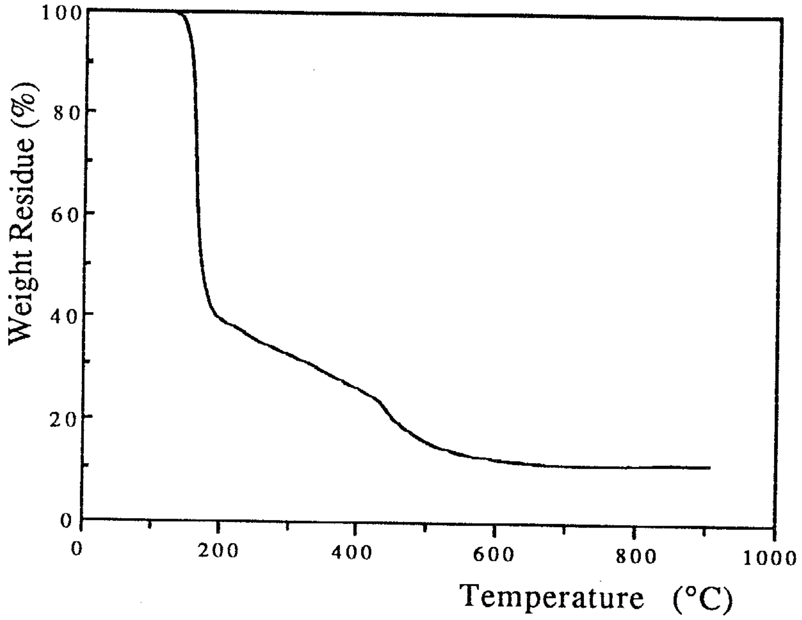


Figure 5 TGA of **3c** under nitrogen.

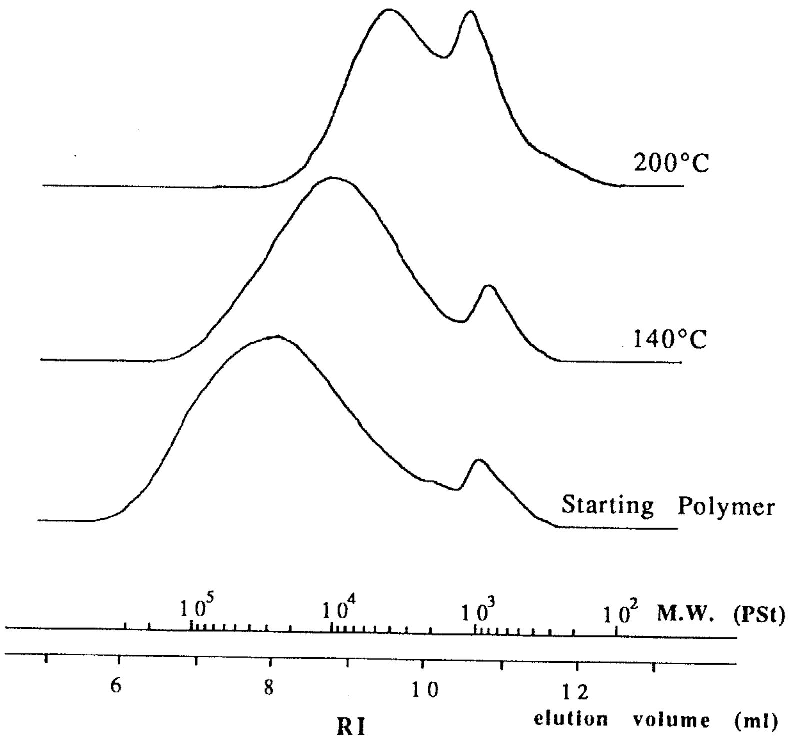


Figure 6 GPC traces of **3c** and the samples after the treatment at 140°C, or 200°C.

Experimental Section

Materials and Instruments. Chloroform was died over phosphorus pentoxide and was distilled before use. Ethanol, benzene, and THF were used as received. **1** (existing as a dimer) was prepared as reported earlier4), and was purified by distillation at 90-92°C/0.1mmHg (lit.5) 98°C/0.12mmHg). **2a**-**2f** were purified by distillation under reduced pressure. **2g** was recrystallized from ethyl acetate.

^{1}H-NMR spectra were recorded in $CDCl_3$ on a Hitachi R-600 instrument (60MHz, tetramethylsilane as an internal standard). ^{11}B-NMR spectra were recorded in $CDCl_3$ on a JEOL JNM-JX-400 instrument (BF_3OEt_2 as an external standard). IR spectra were obtained on a Perkin Elmer 1600 spectrometer. Gel permeation chromatographic analyses were carried out on a Tosoh HLC-8020 (TSK gel G4000) by using THF as an eluent after calibration with standard polystyrene samples. Thermogravimetric analysis (TGA) was made on a Shimadzu DT-30 instrument (15°C/min.) under air or nitrogen stream. Differential scanning carolimetry (DSC) was measured on a Seiko DSC200 instrument (10°C/min.).

Synthesis of 3a-3g from 1 and 2a-3g. To a two-necked flask equipped with magnetic stirrer bar, a septum inlet and a three-way cock, **2a** (0.032g, 0.41mmol), followed by **1** (0.120g, 0.95mmol) were added at room temperature under nitrogen. After 3h at ambient temperature, the reaction product was dissolved in 2ml of THF and precipitated into 30ml of $EtOH/H_2O$ (v/v=1/1). The obtained polymer was freeze-dried with benzene. Yield 0.119g (88%); ^{1}H-NMR (δ, ppm) 0.14-1.60 (*n*-Bu, 36H), 2.48 (N=C-CH_2-, br m 4H), 7.38 (N=CH-, br 2H); IR (neat) 2954, 2917, 2870, 1684, 1459, 1376, 1222, 1098, 934, 798, 735cm^{-1}.

In a similar manner, **3b**-**3g** were obtained. **3b** from 0.047g (0.50mmol) of **2b** and 0.117g (0.93mmol) of **1**; Yield 0.145g (90%); ^{1}H-NMR (δ, ppm) 0.14-1.94 (*n*-Bu, N=C-C-CH_2-, total 38H), 2.29 (N=C-CH_2-, br m 4H), 7.34 (N=CH-, br 2H); IR (neat) 2917, 2868, 1682, 1464, 1376, 1220, 1097, 935, 807, 761cm^{-1}. **3c** from 0.057g (0.53mmol) of **2c** and 0.119g (0.95mmol) of **1**; Yield 0.133g (78%);

^{1}H-NMR (δ, ppm) 0.17-1.86 (*n*-Bu, N=C-C-CH_2-, total 40H), 2.27 (N=C-CH_2-, br m 4H), 7.34 (N=CH-, br 2H); IR (neat) 2954, 2917, 2867, 1684, 1459, 1375, 1302, 1222, 1098, 1022, 935, 804, 733cm^{-1}. **3d** from 0.069g (0.57mmol) of **2d** and 0.116g (0.92mmol) of **1**; Yield 0.131g (77%); ^{1}H-NMR (δ, ppm) 0.14-1.75 (*n*-Bu, -C-CH_2-, total 42H), 2.27 (N=C-CH_2-, br m 4H), 7.38 (N=CH-, br 2H); IR (neat) 2954, 2917, 2869, 1684, 1452, 1376, 1304, 1223, 1097, 963, 933, 808, 772, 736cm^{-1}. **3e** from 0.073g (0.54mmol) of **2b** and 0.118g (0.94mmol) of **1**; Yield 0.138g (76%); ^{1}H-NMR (δ, ppm) 0.14-1.88 (*n*-Bu, -C-CH_2-, total 44H), 2.52 (N=C-CH_2-, br m 4H), 7.38 (N=CH-, br 2H); IR (neat) 2922, 2863, 1684, 1457, 1377, 1301, 1221, 1097, 1022, 939cm^{-1}. **3f** from 0.086g (0.53mmol) of **2f** and 0.114g (0.90mmol) of **1**; Yield 0.159g (85%); ^{1}H-NMR (δ, ppm) 0.10-1.87 (*n*-Bu, -C-CH_2-, total 48H), 2.27 (N=C-CH_2-, br m 4H), 7.34 (N=CH-, br 2H); IR (neat) 2921, 2860, 1684, 1458, 1376, 1301, 1221, 1097, 937, 808, 730cm^{-1}. **3g** from 0.064g (0.50mmol) of **2g** and 0.119g (0.95mmol) of **1**; Yield 0.049g (25%); ^{1}H-NMR (δ, ppm) 0.14-1.94 (*n*-Bu, 36H), 7.23-8.75 (N=CH-, C_6H_4, total 6H); IR (neat) 2954, 2917, 2868, 1701, 1649, 1438, 1373, 1228, 1156, 1097, 796, 690cm^{-1}.

References and Notes

1) Lloyd, J. E.; Wade, K. *J. Chem. Soc.*, **1964**, 1649.
2) No obvious increase of the molecular weight was observed after the reaction for several hours. Therefore, all the reactions were carried out for 1h.
3) See 4-1.
4) (a) Brown, H. C.; Gupta, S. K. *J. Organomet. Chem.*, **1971**, 32, C1.
   (b) Brown, H. C.; Negishi, E.; Gupta, S. K. *J. Am. Chem. Soc.*, **1970**, 92, 6648.
5) Köster, R; Bruno, G.; Binger, P. *Annalen*, **1961**, 644, 1.

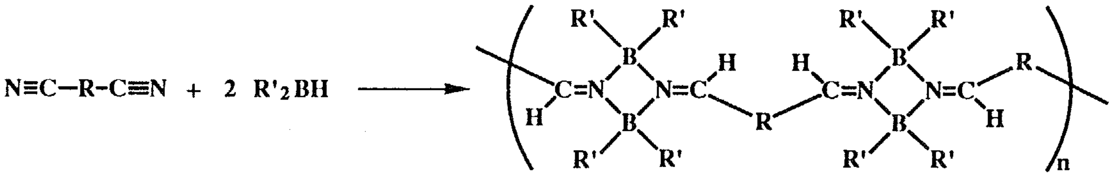
4 - 4

Synthesis of Boron-Containing Polymers by the Reaction between Masked Dialkylboranes and Dicyano Compounds.

Introduction

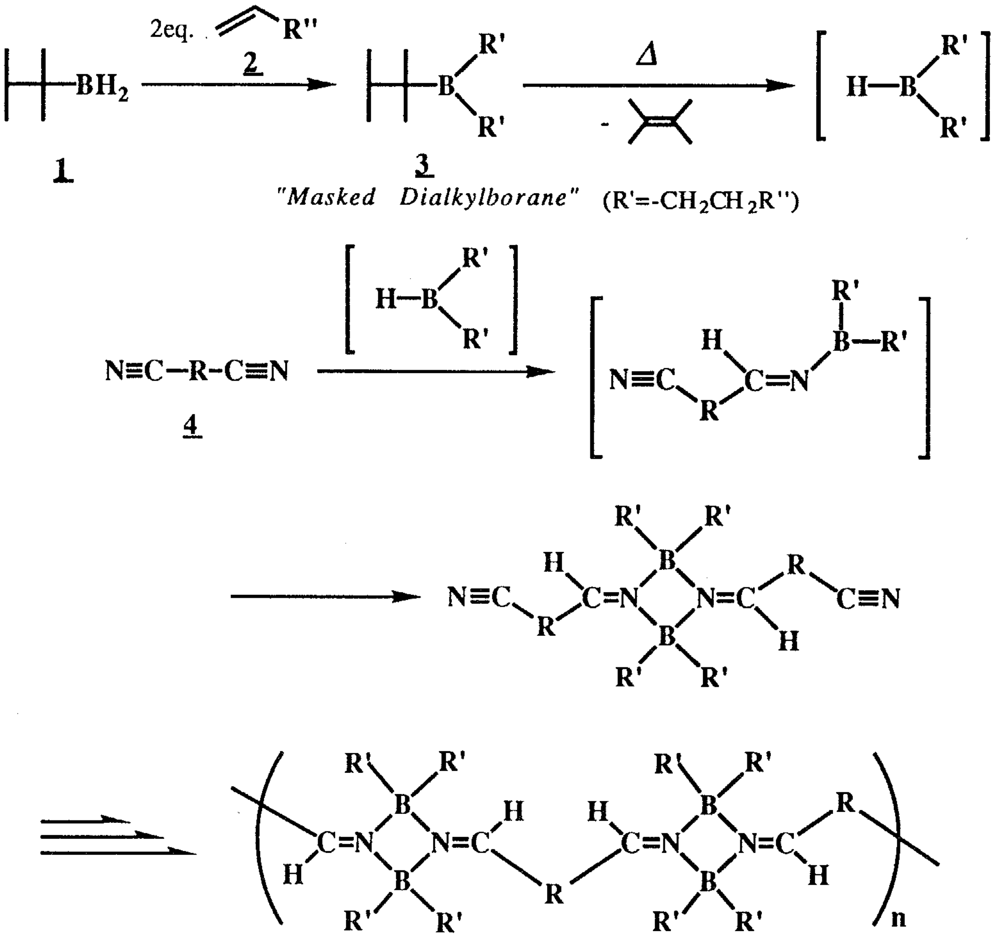
As mentioned in the previous sections, boron-containing polymers bearing boron-nitrogen four-membered rings (i.e., cyclodiborazane) in the main chain can be obtained by the hydroboration reaction of dicyano compounds. The resulting polymers were soluble in common organic solvents and stable under air and moisture. Such stable boron-containing polymers might be attractive for new materials as well as precursors of inorganic materials after pyrolysis1). In the case of the reaction between the isolated dialkylboranes and dicyano compounds, polymers having cyclodiborazane backbone bearing two alkyl groups on each boron atom were obtained (Scheme I)2).

Scheme I



This method, however, requires the isolation of borane monomer, which may limit the substituent on the boron atom. In order to extend the possibilities for the preparation of this type of boron-containing polymers, this section describes the polymerization using masked dialkylboranes and dicyano compounds (Scheme II). Because dialkylthexylborane, which can be easily prepared from thexylborane and olefins, may have a potential to release 2,3-dimethyl-2-butene by the *retro*-hydroboration to produce dialkylborane, the direct use of the masked borane may serve as an alternative and facile method for the synthesis of boron-containing polymers having the same structures as those from isolated dialkylboranes.

Scheme II



Results and Discussion

Previously, the elimination of 2,3-dimethyl-2-butene from alkylthexylboranes was observed in the reactions of thexylmonoalkylboranes with olefins3) or in the treatments of thexylmonoalkylboranes with triethylamine4) (Scheme III). In the latter example, coordination of Lewis base is said to promote the *retro*-hydroboration. If the *retro*-hydroboration of bulky alkyl groups such as thexyl group on the boron atom is achieved in the presence of nitrile compounds, the generated B-H species may attack nitrile groups to produce iminoboranes. Therefore, a direct polymerization reaction of dicyano compounds with dialkylthexylboranes might generate the corresponding dialkylboranes by the *retro*-hydroboration which might participate in hydroboration polymerization.

As dialkylthexylboranes (3) can be obtained almost quantitatively by the hydroboration of terminal olefins with thexylborane (1)$^{5)}$, the hydroboration method was used to obtain the starting masked boranes, and the obtained **3** were used without further purification.

Scheme III

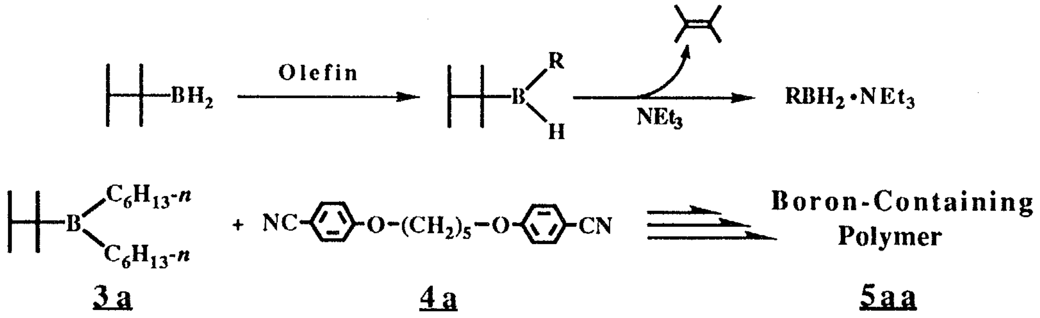


Table I Hydroboration Polymerization between 3a and 4a under Various Reaction Conditions.$^{a)}$

Condition		$\overline{M}_n$ $^{b)}$	$\overline{M}_w$ $^{b)}$	$\overline{M}_w/\overline{M}_n$ $^{b)}$
80°C	4 h	1,430	1,650	1.15
	7 h	1,690	2,210	1.30
100°C	3 h	2,660	4,610	1.73
	5 h	3,130	5,730	1.83
	7 h	2,400	3,940	1.64
120°C	5 h	3,010	5,450	1.81

a) Reactions were carried out in diglyme under the feed ratio of [Borane]/[C≡N]=1.2.

b) GPC (THF), polystyrene standard.

Dependence of Molecular Weight on Reaction Temperature and Time. In order to know the suitable polymerization conditions, the reactions between **4a** and dihexylthexylborane (**3a**) (prepared from **1** and 1-hexene (**2a**)) were carried out in diglyme at various temperatures (e.g., 80, 100 and 120 °C), and the resulting polymers were subjected to GPC analyses after every one hour. Although **3a** should be obtained quantitatively from **1**, the *retro*-hydroboration might not be quantitative. Thus, a little excess of **1** to the cyano group (1.2 eq.)

was used as a monomer formation. The results are summarized in Table I, in which the best result was obtained when the reaction was carried out at 100°C for 5 hours. At 80 °C, the polymer obtained had lower molecular weight presumably due to the insufficient *retro*-hydroboration that supplied B-H species for the polymerization. Because the result at 120 °C was almost same as that at 100 °C, the reaction at lower temperature (100 °C) was chosen for the following studies to prevent side reactions such as additions of B-H species towards iminoboranes and the formation of six-membered rings.

Dependence of Molecular Weight on the Feed Ratio of 4a/1. Generally, stoichiometry is quite important for the step-growth polymerizations6). As shown in Scheme II, the present reaction consists of two reactions. That is, hydroboration of dialkylboranes generated from dialkylthexylboranes (**3**) with dicyano compounds and the dimerization of iminoborane species. In the case of hydroboration polymerization with dialkylborane (in Chapter 11), monomeric iminoboranes could not be detected throughout the polymerization, which may indicate that the dimerization of iminoboranes is faster than hydroboration reaction. On the basis of this supposition, the rate determining step in the present system may be the *retro*-hydroboration or the hydroboration of cyano groups. Therefore, the amount of masked borane for the polymerization might effect the molecular weight of the resulting polymers.

The reactions between **4a** and **3a** (prepared *in situ* from **1** and **2a**) were carried out in diglyme at 100°C for 5 h under various feed ratios of **1**/**4a** (Table II and Figure 1). Among the examined reaction conditions, 2.5 eq. of **1** to the cyano group in **4a** gave the polymer having the highest molecular weight. In the case of isolated dialkylboranes in the previous chapter, no obvious dependence on the feed ratio of two monomers were observed, presumably because the reaction proceeds in two phases. The requirement of an excess of **3a** (i.e., **1**) might indicate that the elimination of 2,3-dimethyl-2-butene from masked borane was not sufficient, and/or the side reactions such as disproportionation of dialkylborane at higher reaction temperature took place. On the other hand, when the ratio of [1]/[C≡N] was higher than 2.5, excess B-H species might attack the carbon-nitrogen double bonds that may produce the undesired dibora-amines.

Table II Hydroboration Polymerization of 4a with 3a under Varied Feed Ratios.[a)]

[3a]/[C≡N]	M_n[b)]	M_w[b)]	M_p[c)]	M_w/M_n
1.0	2,430	3,750	1,520	1.54
1.2	3,130	5,730	4,090	1.83
1.5	3,390	6,400	4,230	1.89
2.0	3,500	8,410	8,450	2.40
2.5	4,290	8,550	7,870	2.00
3.0	4,020	9,120	8,160	2.27
5.0	1,170	1,870	1,600	1.60

a) Reactions were carried out in diglyme at 100°C for 5h.
b) GPC (THF), polystyrene standard.
c) Peak top molecular weight.

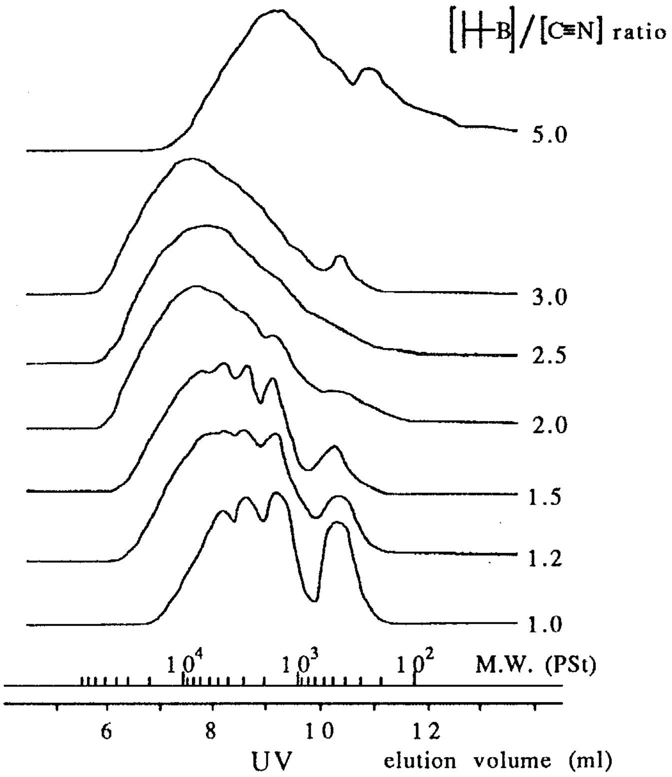


Figure 1 GPC traces for the polymer obtained from 3a and 4a under various feed ratios.

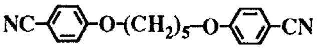
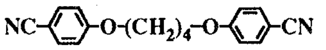
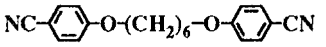
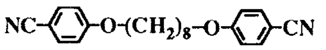
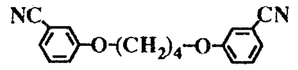
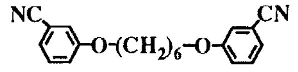
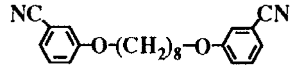
Dependence of Molecular Weight on Monomer Concentration. Effect of initial monomer concentration in diglyme was examined at 100°C for 5 h using 2.5 eq. of **3a** to **4a** in three distinct concentrations (7.8 (bulk), 3.9, and 2.2 M). As shown in Table III, the concentration of 3.9 M gave a polymer having higher molecular weight among the examined concentrations.

Table III Hydroboration Polymerization of 4a with 3a under Varied Feed Concentrations.[a]

[1](mol/L)	M_n	M_w	M_p	M_w/M_n
7.8[b]	2,220	5,640	4,310	2.54
3.9	4,290	8,550	7,870	1.99
2.2	910	1,590	1,410	1.75

a) Reactions were carried out in diglyme at 100°C for 5h under [1]/[CN]=2.5.
b) Reaction was carried out in bulk.

Table IV Synthesis of Boron-Containing Polymers from 3a and Various Aromatic Dicyano Compounds (4a-4i).

Run	Dicyano Compounds		M_n[a]	M_w[a]	Yield[b](%)
1		(4a)	2,200	3,640	26
2		(4b)	2,490	8,890	78
3		(4c)	3,370	13,680	60
4		(4d)	3,220	10,970	66
5		(4e)	1,910	2,520	37
6		(4f)	870	990	33
7		(4g)	1,100	2,690	35

a) GPC (THF), polystyrene standard.
b) Isolated yields after precipitation with EtOH/H_2O (v/v=1/1).

Hydroboration Polymerization between 3a and Various Aromatic Dicyano Compounds (4a-4g). Using a masked borane (**3a**), polymerizations of various aromatic dicyano compounds (**4a**-**4g**) were examined under the conditions as mentioned above (Table IV). From these results, the molecular weights of the obtained polymers (**5aa**-**5ag**) seemed to be regardless to the number of methylenes in dicyano monomers (**4a**-**4d**). α,ω-Bis(cyanophenoxy)alkanes, in which cyano groups are bonded at *p*-position always gave polymers having higher molecular weights in higher yields than those having cyano groups at *m*-position (**4b** vs. **4e**, **4c** vs. **4f**, and **4d** vs. **4g**). In the IR spectra of **5aa**-**5ag**, strong absorptions around 1643cm^{-1} attributable to C=N stretching vibration of dimeric iminoboranes were observed.

Hydroboration Polymerization between 3a and Aliphatic Dicyano Compounds (4h-4l). Since aliphatic dicyano compounds used here were liquid, the reaction mixture became homogeneous without any added solvents. Accordingly, unlike aromatic dicyano compounds, reactions were carried out in bulk7). As shown in Table V, the corresponding polymers (**5ah**-**5al**) were obtained in moderate yields, whose IR spectra indicated C=N stretching absorption of dimeric iminoboranes around 1673cm^{-1}.

Table V Hydroboration Polymerization of Various Aliphatic Dicyano Compounds (4h-4l) with 3a.a)

Run	Dicyano Compounds	Boron-Containing Polymers			
			$\overline{M}_n$ b)	$\overline{M}_w$ b)	Yield(%)c)
1	$NC(CH_2)_3CN$ (4h)	(5ah)	1,370	3,810	58
2	$NC(CH_2)_4CN$ (4i)	(5ai)	3,640	26,880	57
3	$NC(CH_2)_5CN$ (4j)	(5aj)	1,650	6,720	49
4	$NC(CH_2)_6CN$ (4k)	(5ak)	2,220	5,640	—
5	$NC(CH_2)_8CN$ (4l)	(5al)	2,340	6,140	59

a) Reactions were carried out in bulk at 100°C for 3h.
b) GPC (THF), polystyrene standard.
c) Isolated yield after precipitation into EtOH/H_2O (v/v=1/1).

Hydroboration Polymerization between 4a and Various Masked Dialkylboranes (3b-3d). In a similar manner to **3a**, dialkylthexylboranes (**3b**-**3d**) were prepared from **1** and 1-octene (**2b**), 4-methylstyrene (**2c**), and allylbenzene (**2d**), respectively, and were used for the following polymerization reactions with **4a** (Table VI), from which the corresponding polymers (**5aa**-**5da**) were obtained in good yields. As a typical example, ^{1}H-NMR and IR spectra of the polymer (**5ca**) obtained from **3c** and **4a** are shown in Figure 2 and Figure 3, respectively.

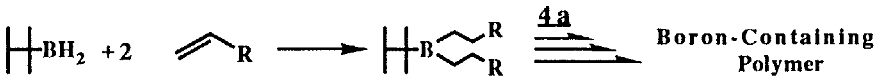
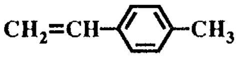
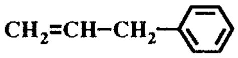


Table VI Hydroboration Polymerization between 4a and Various Dialkylthexylboranes (3a-3d).

Run	Olefin		Condition$^{a)}$	Polymer		
					Yield(%)$^{b)}$	$\overline{M}_n$$^{c)}$
1		(2a)	A	(5aa)	78	2,490
2		(2b)	A	(5ba)	94	5,650
3		(2c)	B	(5ca)	81	4,750
4		(2d)	B	(5da)	62	5,670

a) Condition A ; 100°C 5h in diglyme, Condition B ; 100°C 3h in bulk.
b) Isolated yields after precipitation into $EtOH/H_2O$ (v/v=1/1).
c) GPC (THF), polystyrene standard.

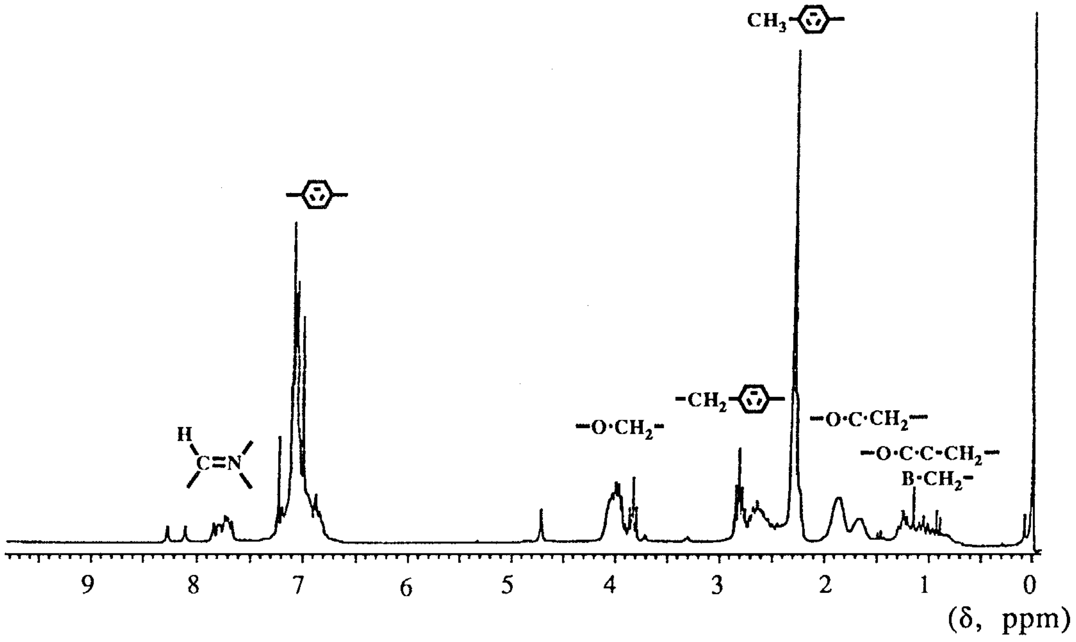


Figure 2 ^{1}H-NMR spectrum of boron-containing polymer (5ca) prepared from 3c and 4a.

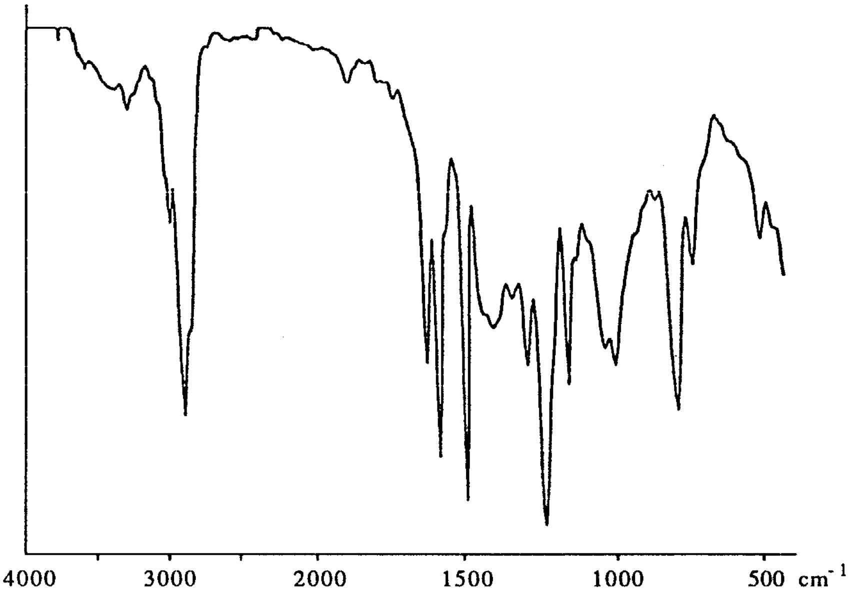


Figure 3 IR spectrum of 5ca.

In comparison with polymers obtained from isolated dialkylborane, polymers obtained from masked borane had somewhat lower molecular weights partly because the reaction requires higher temperature. However, the present method might be served as an alternative and facile synthetic way to obtain boron-containing polymers having various substituents on the boron atom.

Experimental Section

Materials and Instruments. **1** was prepared by the reaction of borane-dimethyl sulfide with 2,3-dimethyl-2-butene, according to the reported method[8]), and was purified by distillation[9]). **2a**-**2d** and **4h**-**4l** were purified by distillation. Tetrahydrofuran and diglyme were dried over sodium and distilled before use. *N*,*N*-Dimethylformamide (DMF) was dried over calcium hydride and distilled before use.

^{1}H-NMR spectra were recorded in $CDCl_3$ on a Hitachi R-600 or Varian Gemini-200 instrument. ^{11}B-NMR spectrum was recorded in $CDCl_3$ on a JEOL JNM-GX400 instrument. IR spectra were obtained on a Perkin Elmer 1600 spectrometer. Gas chromatographic analysis was made on a Shimadzu GC-6A instrument. Gel permeation chromatographic analyses were carried out on a Tosoh HLC-8020 (TSK gel G3000) by using THF as an eluent after calibration with standard polystyrene samples.

Synthesis of Monomers (4a-4g). As a typical procedure, synthesis of 1,5-bis(4,4'-cyanophenoxy)pentane (**4a**) is described as follows: To a 25ml DMF solution of 4-cyanophenol (6.03g, 50.6mmol) and 1,5-dibromopentane (6.13g, 26.7mmol), sodium carbonate (6.90g, 65.1mmol) was added. The mixture was stirred overnight at 100°C and was poured into aqueous sodium hydroxide (1N). The precipitate was filtered and washed with H_2O and EtOH several times. The recrystallization from *n*-hexane gave **4a** as a white crystal. Yield 3.80g (60%); mp. 112.5-113.5°C; ^{1}H-NMR (δ, ppm) 1.43-2.30 (CH_2, m, 6H), 4.07 (OCH_2, t, 4H), 6.77-7.77 (C_6H_4, m, 8H); IR (KBr) 2955, 2876, 2221, 1606, 1509, 1471, 1301, 1262, 1173, 1007, 836cm^{-1}.

Dicyano monomers (**4b-4g**) were obtained in a similar way. **4b**: Yield 67%; mp. 169.5-170.5°C; ^{1}H-NMR (δ, ppm) 1.74-2.28 (CH_2, m, 4H), 4.09 (OCH_2, t, 4H), 6.68-7.83 (C_6H_4, m, 8H); IR (KBr) 2954, 2889, 2224, 1605, 1507, 1300, 1256, 1175, 1006, 831cm^{-1}. **4c**: Yield 51%; mp. 143-144°C; ^{1}H-NMR (δ, ppm) 1.31-2.14 (CH_2, m, 8H), 4.03 (OCH_2, t, 4H, J=6Hz), 6.70-7.81 (C_6H_4, m, 8H); IR (KBr) 2943, 2867, 2213, 1600, 1507, 1306, 1262, 1175, 1011, 837cm^{-1}. **4d**: Yield 39%; mp. 128-129°C; ^{1}H-NMR (δ, ppm) 1.08-2.06 (CH_2, m, 12H), 3.99 (OCH_2, t, 4H, J=5.5Hz), 6.69-7.94 (C_6H_4, m, 8H); IR (KBr) 2932, 2867, 2224, 1605, 1507, 1300, 1256, 1169, 1022, 837cm^{-1}. **4e**: Yield 22%; mp. 122.5-123.5°C; ^{1}H-NMR (δ, ppm) 1.39-2.60 (CH_2, m, 4H), 4.05 (OCH_2, t, 4H), 6.36-7.89 (C_6H_4, m, 8H); IR (KBr) 2932, 2867, 2224, 1589, 1480, 1436, 1262, 1164, 1049, 995, 870, 782cm^{-1}. **4f**: Yield 55%; mp. 102-103°C; ^{1}H-NMR (δ, ppm) 1.05-2.12 (CH_2, m, 8H), 3.99 (OCH_2, t, 4H), 6.73-7.70 (C_6H_4, m, 8H); IR (KBr) 2943, 2867, 2224, 1578, 1480, 1289, 1262, 1148, 1033, 870, 788cm^{-1}. **4g**: Yield 21%; mp. 86-87°C; ^{1}H-NMR (δ, ppm) 1.20-2.06 (CH_2, m, 12H), 3.97 (OCH_2, t, 4H, J=5.5Hz), 6.99-7.73 (C_6H_4, m, 8H); IR (KBr) 2929, 2863, 2225, 1578, 1480, 1442, 1289, 1256, 1142, 1039, 886, 782cm^{-1}.

Polymerization. Dependence of Molecular Weight on Temperature and Time (Table I). The reaction condition was examined by using **4a**. General procedure is described as follows: To a 1.2ml THF solution (1.3M) of **1** (1.57mmol), 0.8ml of **2a** was added under nitrogen at 0°C. After 1h stirring at that temperature, the solvent and unreacted **2a** were evaporated under vacuum, followed by the addition of 0.2ml of diglyme. To the solution of **3a** thus obtained, **4a** (0.200g, 0.65mmol) was added. The solution was heated at 80°C and GPC analyses were subjected after every one hour. Similarly, GPC analyses were subjected to the samples prepared at 100 and 120°C. The results are summarized in Table I.

Dependence of Molecular Weight on the Feed Ratio of 1/4a (Table II, Figure 1). General procedure is described as follows: To a diglyme solution of dihexylthexylborane prepared as mentioned above, **4a** was added under nitrogen at 0°C. The solution was heated to 100°C and was kept stirring at that temperature. GPC analysis was subjected directly after 5h. The feed ratios and the results of GPC analyses are illustrated in Figure 1 and Table II, in which the feed ratios are indicated by the ratios of **1** to cyano groups in **4a**.

Dependence of Molecular Weight on Monomer Concentration (Table III). General procedure is described as follows: The amount of diglyme added to **3a** (about 1.57mmol, prepared as mentioned above) was varied from 0ml (bulk) to 0.5ml (2.2M). In any case, an equimolar amount of **4a** was added under nitrogen. The reaction mixture was heated to 100°C and was stirred at that temperature. After 5h, GPC analyses were subjected directly.

Hydroboration Polymerization between 3a and 4a. To a diglyme solution of **3a** (about 1.57mmol) prepared from **1** (0.153g, 1.57mmol) as mentioned above, **4a** (0.0962g, 0.314mmol) was added under nitrogen at 0°C. The solution was heated to 100°C and was reacted at that temperature for 5h. The obtained product was reprecipitated into $EtOH/H_2O$ (v/v=1/1) and was freeze-dried from benzene. **5aa**: Yield 0.164g (78%); ^{1}H-NMR (δ, ppm) 0.31-1.02 (CH_3, BCH_2, m, 20H), 1.02-1.55 (CH_2, m, 34H), 1.55-2.18 (O-C-CH_2, m, 4H), 3.85-4.05 (OCH_2, m, 4H), 6.68-8.09 (C_6H_4, m, 8H), 8.29 (N=CH, br, s, 2H); IR (film) 2918, 2863, 1689, 1645, 1601, 1508, 1310, 1255, 1167, 1024, 826cm^{-1}.

Similarly, **5ab**-**5ag** were obtained as follows: **5ab**: Yield 26%; ^{1}H-NMR (δ, ppm) 0.41-1.04 (CH_3, BCH_2, m, 20H), 1.04-1.63 (CH_2, m, 32H), 1.63-2.33 (O-C-CH_2, m, 4H), 3.84-4.34 (OCH_2, m, 4H), 6.59-8.30 (C_6H_4, m, 8H), 8.40 (N=CH, br, s, 2H); IR (film) 2918, 2863, 1645, 1607, 1508, 1354, 1255, 1173, 1046, 826cm^{-1}. **5ac**: Yield 60%; ^{1}H-NMR (δ, ppm) 0.35-1.06 (CH_3, BCH_2, m, 20H), 1.06-2.16 (CH_2, m, 40H), 3.55-4.30 (OCH_2, m, 4H), 6.55-8.08 (C_6H_4, m, 8H), 8.28 (N=CH, br, s, 2H); IR (film) 2915, 2863, 1687, 1646, 1605, 1512, 1304, 1255, 1021, 834cm^{-1}. **5ad**: Yield 66%; ^{1}H-NMR (δ, ppm) 0.35-1.02 (CH_3, BCH_2, m, 20H), 1.02-1.64 (CH_2, m, 40H), 1.64-2.21(O-C-CH_2, m, 4H), 3.24-4.38 (OCH_2, m, 4H), 6.55-8.55 (C_6H_4, m, 8H), 8.30 (N=CH, br, s, 2H). **5ae**: Yield 37%; IR (film) 2907, 2863, 1640, 1590, 1475, 1436, 1381, 1326, 1261, 1151, 1046, 865, 782cm^{-1}. **5af**: Yield 33%; IR (film) 2940, 2863, 1645, 1590, 1480, 1431, 1326, 1261, 1145, 1019, 865, 788cm^{-1}. **5ag**: Yield 35%; IR (film) 2918, 2852, 1645, 1596, 1447, 1414, 1266, 1156, 1041, 876, 782cm^{-1}.

Hydroboration Polymerization between 3a and 4h-4l. Since most of aliphatic dicyano compounds were liquid monomers, the reactions were carried out in bulk. The reaction condition was examined by using **4k**. In a similar manner to the case of **4a**, **3a** (about 1.47 mmol) prepared from **1** and **2a**, and **4k** (0.0417g, 0.306mmol) were reacted at 100°C under nitrogen, and GPC were measured after every one hour. The results of the GPC measurements are as follows; 1h: M_n=1,910, M_w/M_n=3.09, 2h: M_n=2,960, M_w/M_n=6.17, 3h: M_n=3,370, M_w/M_n=5.49, 4h: M_n=2,630, M_w/M_n=4.61, and 5h: M_n=2,630, M_w/M_n=4.91. From these results, reactions of aliphatic dicyano compounds with **3a** were carried out in bulk at 100°C for 3h.

Similarly, boron-containing polymers were prepared and were isolated by the reprecipitation with EtOH/H_2O (v/v=1/1). **5ah**: Yield 58%; IR (film) 2918, 2852, 1645, 1596, 1447, 1414, 1266, 1156, 1041, 876, 782cm^{-1}. **5ai**: Yield 57%; ^{1}H-NMR (δ, ppm) 0.60-1.60 (CH_3, BCH_2, m, 20H), 1.60-1.83 (CH_2, m, 36H), 1.83-2.93(N=C-CH_2, m, 4H), 7.28 (N=CH, br, s, 2H). **5aj**: Yield 49%; IR (film) 2918, 2852, 1684, 1458, 1381, 1261, 1206, 1107, 1019, 892, 804cm^{-1}. **5al**: Yield 59%; ^{1}H-NMR (δ, ppm) 0.43 (BCH_2, t, 8H), 0.86(CH_3, t, 12H), 1.00-1.80 (CH_2, m, 44H), 1.80-2.57(N=C-CH_2, m, 4H), 7.30 (N=CH, br, s, 2H); ^{11}B-NMR (δ, ppm) 5.5ppm; IR (film) 2918, 2852, 1684, 1464, 1376, 1261, 1206, 1107, 1013, 810cm^{-1}.

Hydroboration Polymerization between 3b-3d and 4a. The reaction of **3b-3d** with **4a** was carried out in a similar manner to the case of **3a** except for using **2b** in place of **2a**. **5ba**: Yield 94%; ^{1}H-NMR (δ, ppm) 0.37-1.05 (CH_3, BCH_2, m, 20H), 1.05-2.15 (CH_2, m, 54H), 3.45-4.29 (OCH_2, m, 4H), 6.63-8.03 (C_6H_4, m, 8H), 8.28 (N=CH, br, s, 2H); IR (film) 2918, 2852, 1695, 1645, 1607, 1513, 1464, 1310, 1261, 1173, 1024, 832, 722cm^{-1}. **5ca:** Yield 0.185g (62%); ^{1}H-NMR (δ, ppm) 0.31-1.08 (BCH_2, m, 8H), 1.08-2.21 (CH_2, m, 14H), 2.21-3.00 ($ArCH_2$, m, 8H), 3.35-4.30 (OCH_2, m, 4H), 6.06-7.84 (ArH, m, 28H), 8.28 (N=CH, br, s, 2H); IR (film) 2929, 2863, 1640, 1601, 1508, 1453, 1305, 1250, 1173, 1068, 1030, 832cm^{-1}. **5da:** Yield 81%; ^{1}H-NMR (δ, ppm) 0.78-1.88(CH_2, m, 14H), 2.29 ($ArCH_3$, s, 12H), 2.75-2.90 ($ArCH_2$, t, 8H), 3.90-4.15 (OCH_2, t, 4H), 6.47-7.27(C_6H_4, m, 16H), 7.37-8.24 (N=CH, m, 2H); IR (film) 2918, 1645, 1607, 1513, 1420, 1310, 1255, 1173, 1030, 815cm^{-1}.

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(b) Narula, C. K.; Paine, R. T.; Schaeffer, R., p378; Shaw, S. Y.; DuBois, D. A.; Neilson, R. H., p385; Paciorek, K. J. L.; Krone-Schmidt, W.; Harris, D. H.; Kratzer, R. H.; Wynne, K. J., p392. In *Inorganic and Organometallic Polymers*; Zeldin, M.; Wynne, K. J.; Allcock, H. R., Eds.; ACS Symposium Series 360; American Chemical Society, Washington, DC, **1988**.

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3) Brown, H. C.; Katz, J-J.; Lane, F.; Negishi, E. *J. Am. Chem. Soc.*, **1975**, 97, 2799.

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5) Especially, hydroboration reactions of **1** with terminal olefins are known to give dialkylthexylboranes in high yields without elimination of thexyl group *via* the *retro*-hydroboration. See, for example; Negishi, E.; Brown, H. C. *Synthesis,* **1974**, 77.
6) Solomon, D. H. *Step-Growth Polymerization*; Marcel Dekker Inc.; New York, 1972.
7) Similarly to the case of aromatic dicyano monomers, reactions were carried out under various reaction conditions, from which polymerization at 100°C for 3 h using a small excess of borane monomer ([**1**]/[C≡N]=2.5) gave the best results (see also Experimental Section). Therefore, the reactions between **3a** and **4h**-**4l** were carried out under these conditions.
8) Brown, H. C.; Mandal, A. K.; Kulkarni, S. U. *J. Org. Chem.*, **1977**, 42, 1392.
9) See 2-1.

Chapter 5

Allylboration Polymerization of Dicyano Compounds and an Alternative Polymerization Reaction

ABSTRACT

Novel boron-containing polymers were obtained by the polyaddition between dicyano compounds and allylboranes such as triallylborane, trimethallylborane, and allyldialkylboranes. In all cases, polymers were obtained in high yields. The rate of polymerization is largely effected by the structure of borane monomers as well as dicyano compounds. The stability of boron-containing polymers was also effected by the structure of the borane monomers. Polymers from triallylborane became insoluble under the storage of the sample for several days, while those from allyldialkylboranes were stable enough under air at least for several months. Similarly to the polymers prepared by the hydroboration polymerization of dicyano monomers, these polymers gave some residue after pyrolysis. For the alternative method to obtain boron-containing polymers, condensation reactions of bis(silylimine)s with substituted boranes such as chlorodialkylborane and methyl dialkylborinates are also described.

In 5-1, polymerization with triallylborane is described. When polymerization between triallylborane and isophthalonitrile was carried out in bulk at 0°C, the reaction mixture became homogeneous liquid within several minutes. After the reaction for 1 day, a glassy polymer was obtained. The molecular weight of the resulting polymer was estimated by GPC, from which M_n and M_w were found to be 14,000, and 25,700, respectively. The structure of the polymer was confirmed by ^{1}H-, ^{11}B-NMR, and IR analyses. The air- as well as thermal stabilities of the obtained polymers were examined. Most part of the resulting boron-containing polymers became insoluble upon the storage even under the inert atmosphere. By heating the polymer around 140°C, an irreversible chemical reaction (i.e., further allylboration reaction) took place and the polymer became insoluble accompanying its structural change.

In 5-2, allylboration polymerization was examined with trimethallylborane. When polymerizations of α,ω-dicyanoalkanes were carried out in bulk at ambient temperature, the allylboration reactions were completed instantly, but the molecular weights of the resulting polymers increased very slowly. The slow rate of

polymerization in comparison with that of triallylborane was responsible for the slow dimerization of sterically hindered iminoboranes. In the case of aromatic dicyano monomers such as isophthalonitrile, the reaction with triallylborane produced oligomers as a result of the insufficient dimerization that could be clearly followed by its IR measurement. The structures of the obtained polymers were confirmed by their spectroscopic measurements. The boron-containing polymers from trimethallylborane were found to be somewhat stable in comparison with those obtained from triallylborane.

Boron-containing polymers obtained in 5-1 and 5-2 were rather unstable due to the remaining reactive allyl group. In order to know the difference of the stability of the resulting polymers as well as to investigate difference of polymerization behavior, in 5-3, allylboration polymerizations were carried out with allyldialkylboranes. For instance, the reaction of allyldi-*n*-hexylborane with adiponitrile in bulk gave a colorless gum in 72% yield (M_n=27,300). The obtained polymer was confirmed to have cyclodiborazane backbone by the results of the spectroscopic measurements. The boron-containing polymers prepared from allyldialkylboranes were much stable in comparison with those prepared from triallylborane or trimethallylborane.

5-4 describes an alternative method to obtain boron-containing polymers having similar structures by the condensation reactions of bis(silylimine)s with substituted boranes such as chlorodialkylborane and methyl dialkylborinates. From the derivatives of di-*n*-alkylboranes and bis(silylimine)s derived from dialdehyde, the corresponding polymers bearing boron-nitrogen four-membered structures in the main chains were produced. The obtained polymers, however, became insoluble after keeping under air. On the other hand, when bis(silylimine)s derived from anthraquinone or sterically hindered boranes were used as a monomer, no polymerization took place and monomeric iminoboranes were produced.

5 - 1

Synthesis of Boron-Containing Polymers by the Reaction between Triallylborane and Dicyano Compounds.

Introduction

Boron-containing polymers bearing borazine, phosphinoborane, decarborane monomer units[1)] have been of interest as polymeric materials or precursors for the production of inorganic materials[2)]. In the preceding chapter, the author has described the synthetic method of novel boron-containing polymers having cyclodiborazane backbones by hydroboration polymerization between monoalkylboranes[3a)] or dialkylboranes[3b)] and dicyano compounds. Polymers obtained by these systems were stable enough against air and water, and gave some residue after pyrolysis. As another method for the preparation of this type of boron-containing polymers, polymerization using allylboration reaction of nitrile groups (i.e., "Allylboration Polymerization") was examined in this section.

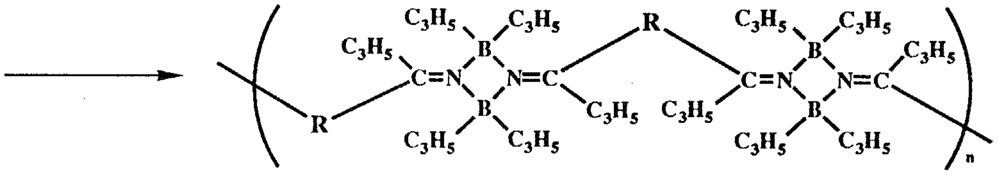
Results and Discussion

The reactions between nitriles and allylboranes such as triallylborane[4)], allyldialkylboranes[5)] were reported to produce derivatives of cyclodiborazanes in quantitative yields. Mikhailov *et al.* have shown that these crystalline compounds were stable under air. As the first trial to obtain boron-containing polymers using allylboration reaction of nitrile groups, polymerization between triallylborane and dicyano compounds was examined here (Scheme I).

When two molar equivalents of triallylborane (**1**) was added to isophthalonitrile (**2a**) without solvent at 0°C under nitrogen, and stirred at room temperature, **2a** dissolved at the early stage[6)], and within a few hours, the reaction mixture became viscous and a colorless glassy product was formed. After dissolving into THF, a polymer (**3a**) was obtained in 78% yield by the reprecipitation into EtOH/H_2O (v/v=1/1). The molecular weight of the obtained polymer was measured by GPC on the basis of polystyrene calibration curves. From this result, M_n and M_w of **3a** were found to be 14,000 and 25,700, respectively.

Scheme I

$2\ B(CH_2CH{=}CH_2)_3 + N{\equiv}C{-}R{-}C{\equiv}N$



The structure of **3a** was confirmed by ^1H-, ^{11}B-NMR, and IR analyses. In its ^1H-NMR spectrum (Figure 1), the peaks assignable to the methylenes adjacent to boron, those adjacent to imino carbon, vinyl protons, and aromatic protons were observed at 0.58-2.26, 3.41, 4.46-6.30, and 6.88-7.62 ppm, respectively. The integral ratios of these peaks were in good agreement to those for the expected structure.

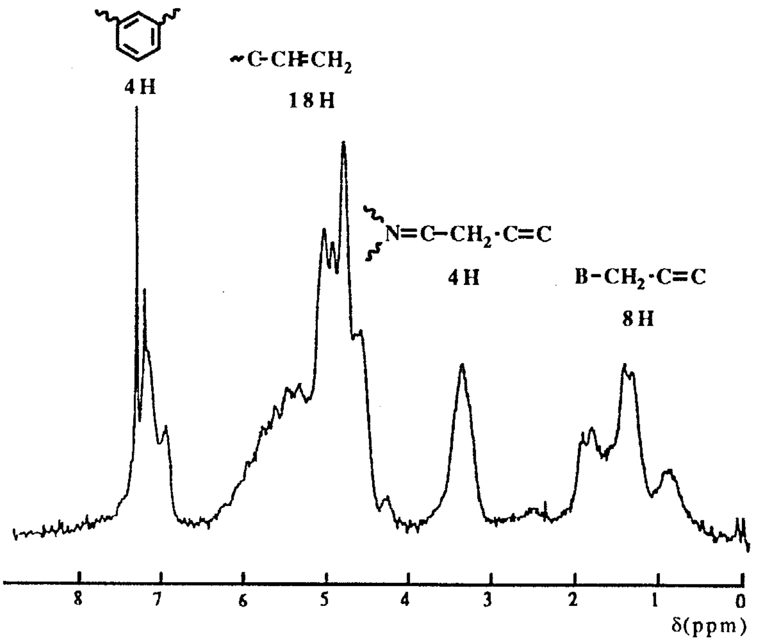


Figure 1 ^1H-NMR spectrum of the boron-containing polymer (3a).

In the ^{11}B-NMR spectrum of **3a**, a broad peak at 3.7ppm accompanying small peaks at 33.2 and 38.1ppm was observed (Figure 2). The ^{11}B-NMR spectrum of an iminoborane dimer (**4**) prepared from benzonitrile and **1** (Scheme II) showed a single peak at 5.0ppm, which was characterized as a four-coordinated boron atom in the four-membered structure. The main peak at 3.7ppm for **3a**, thus, supported the formation of a four-membered structure. The small peaks at 33.2 and 38.1ppm might be ascribed to the three coordinated monomeric iminoborane species[7)] (i.e., chain-end of the boron-containing polymer) or some impurities.

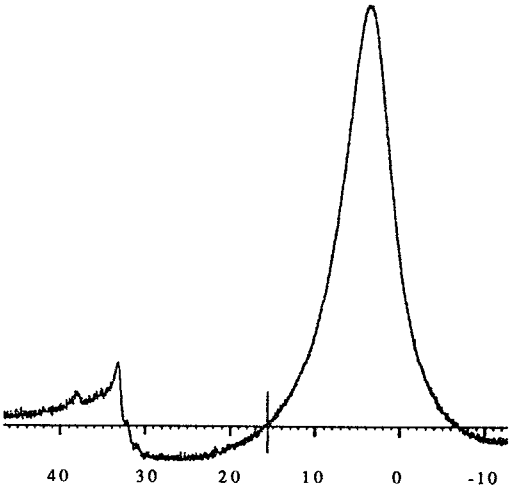


Figure 2 ^{11}B-NMR spectrum of **3a**.

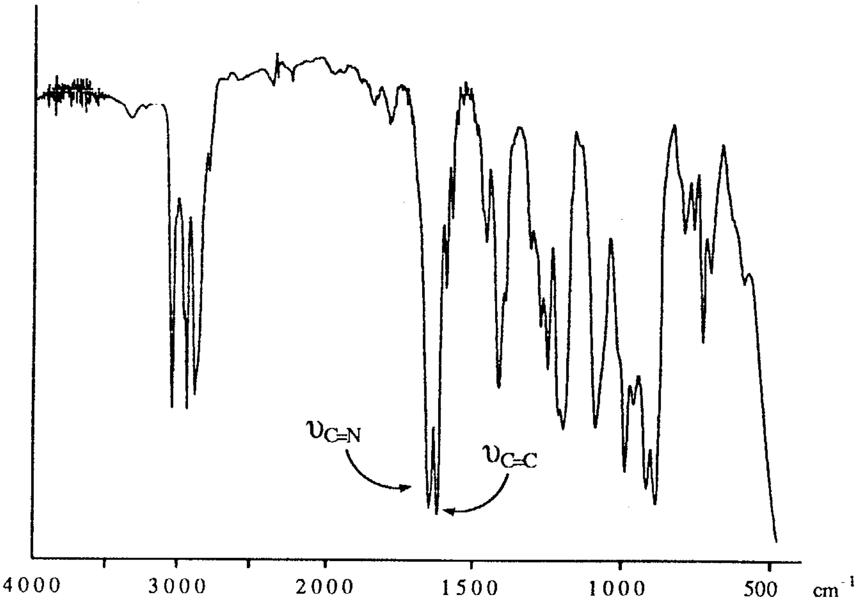


Figure 3 IR spectrum of **3a**.

In its IR spectrum (Figure 3), a strong peak due to the dimeric form of iminoborane (C=N stretching) was observed at 1659cm^{-1}. No peak was observed at 2240cm^{-1}, which indicated the complete conversion of C≡N.

Polymerizations of various dicyano compounds with **1** were examined under the same conditions. The results are summarized in Table I. Aliphatic dicyano compounds (**2c**-**2h**) as well as aromatic dicyano compounds (**2a**, **2b**) resulted in the formation of the corresponding boron-containing polymers in good yields. All polymers obtained here were soluble in common organic solvents such as THF, $CHCl_3$, and benzene.

Table I Allylboration Polymerization of Various Dicyano Compounds with Triallylborane.[a)]

Run	Dicyano Compounds		Yield[b)] (%)	$\overline{M}_n$[c)]	$\overline{M}_w$[c)]
1	m-NC-C_6H_4-CN	(**2a**)	78	14,000	25,700
2	p-NC-C_6H_4-CN	(**2b**)	89	5,900	11,000
3	$NC(CH_2)_2CN$	(**2c**)	79	4,500	9,200
4	$NC(CH_2)_3CN$	(**2d**)	78	5,500	12,000
5	$NC(CH_2)_4CN$	(**2e**)	81	6,300	13,600
6	$NC(CH_2)_5CN$	(**2f**)	93	8,900	18,000
7	$NC(CH_2)_6CN$	(**2g**)	85	9,000	20,400
8	$NC(CH_2)_8CN$	(**2h**)	89	11,900	24,600

a) Polymerizations were carried out in bulk at 0°C.
b) Isolated yields after precipitation into $EtOH/H_2O$ (1/1).
c) GPC (THF), polystyrene standard.

Thermogravimetric analyses (TGA) of **3a** were carried out under nitrogen and under air (Figure 4). In both cases, a black solid was left in 38% after pyrolysis at 900°C. This result might be taken that boron-containing polymers obtained here can be expected as precursors for boron-containing inorganic materials.

Differential scanning calorimetric analysis (DSC) of **3a** gave a significant information about the thermal reaction of **3a** (Figure 5). At the first scan of **3a**, a strong exothermic peak at 140°C was recognized. At the second scan, however, the corresponding peak was not observed. The samples after the DSC measurement were insoluble in THF, $CHCl_3$, or benzene. From the results of IR measurement, no peak for iminoborane species was detected[8]. It is known that **4** is changed to **5** by the further intramolecular allylboration reaction upon heating at 100°C for 1h[4b] (Scheme II). These facts suggest that the thermal treatment of **3a** caused the further allylboration reaction to form a polymer consisting of new B-N four-membered rings (i.e., cycloboratizine backbones). The low solubility of the polymer obtained after the heating might be caused by some intermolecular crosslinking reactions *via* a thermal allylboration reaction (Scheme III).

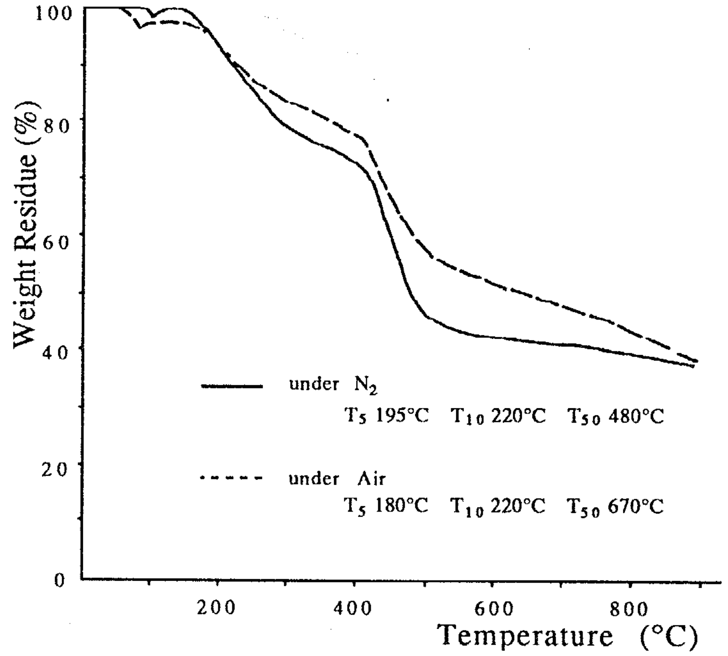
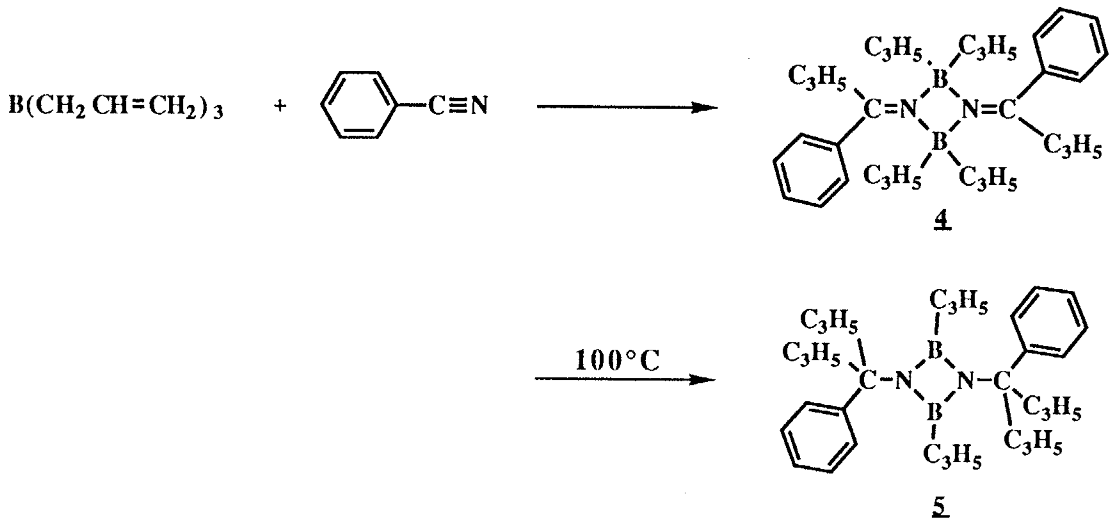


Figure 4 Thermogravimetric analysis of 3a.

Scheme II



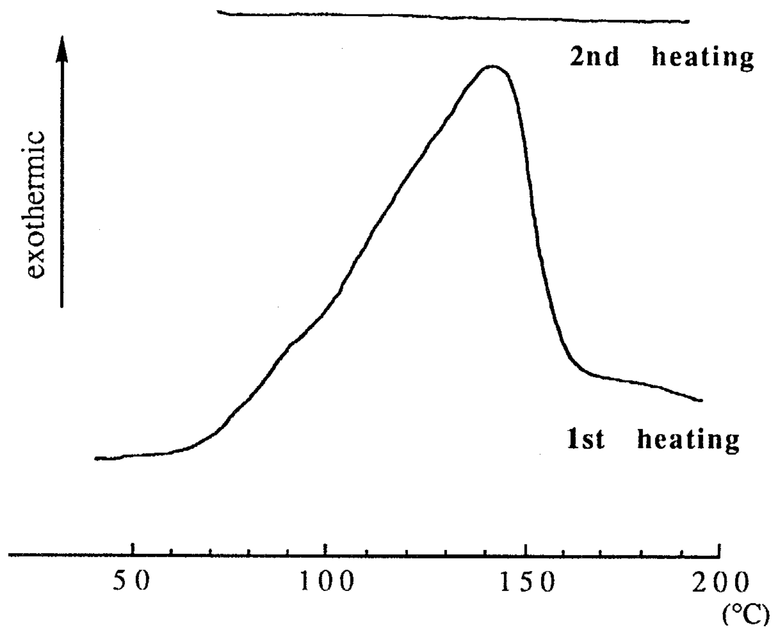
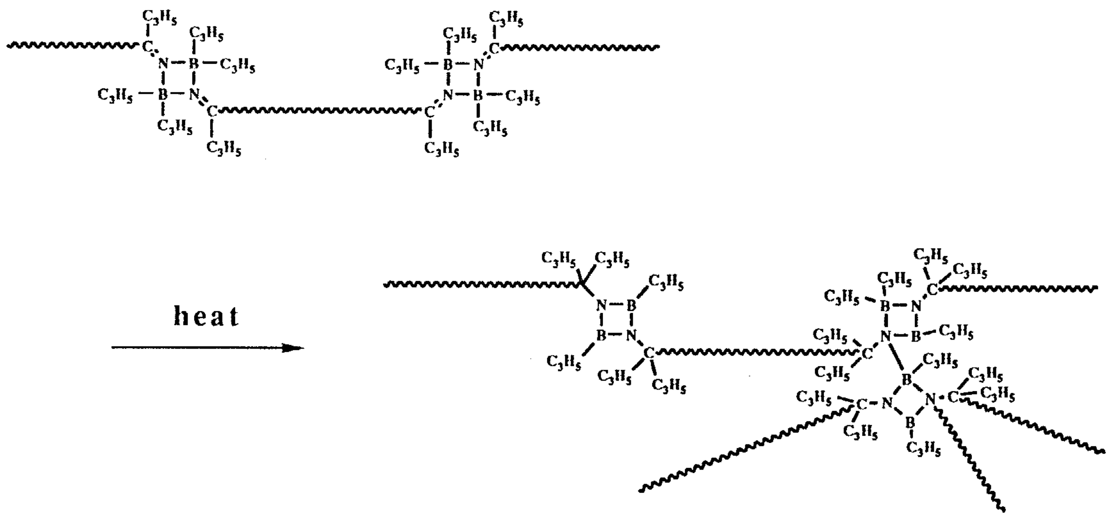


Figure 5 Differential scanning calorimetric analysis of 3a.

Scheme III



The air stability of 3a was monitored by tracing the change of its molecular weight in GPC on exposure to the air for several days (Figure 6). When the sample was kept under air for several days, it became less soluble, and the molecular weight of the THF-soluble part was lower in comparison with that of the sample freshly prepared. Even kept under nitrogen, the same change was observed. Thus, this might be also partly caused by the crosslinking reaction similar to the thermal reaction.

Although, it was found that the polymers obtained by the allylboration polymerization with **1** were rather unstable under the storage, these polymers might be served as new materials and/or as precursors for inorganic materials.

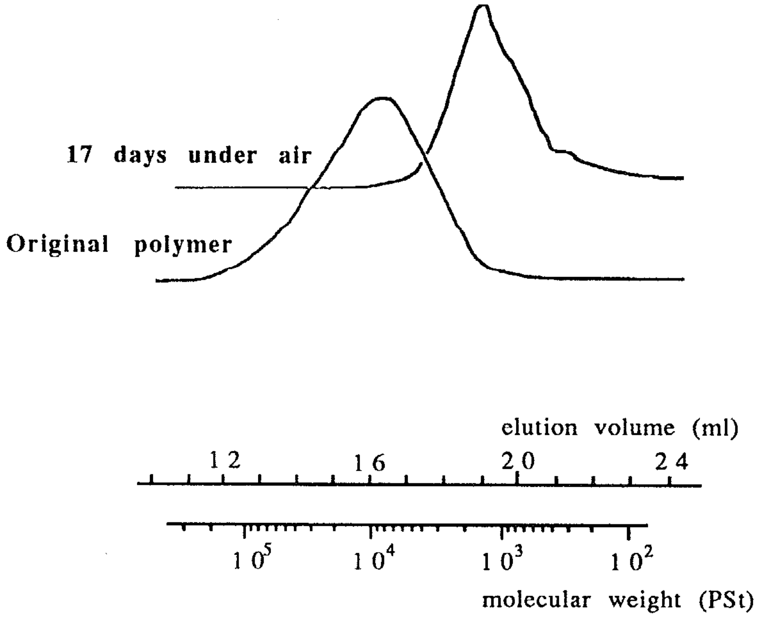


Figure 6 Stability of 3a under air.

Experimental Section

Materials and Instruments. Chloroform was dried over phosphorus pentoxide and was distilled before use. Ethanol, benzene, and THF were used as received. **1** was prepared as reported earlier9), and purified by distillation under nitrogen. **2a** and **2b** were recrystallized from ethyl acetate and methanol, respectively. **2c**-**2h** were purified by distillation under reduced pressure.

^{1}H-NMR spectra were recorded in CDCl$_3$ on a Hitachi R-600 instrument (60MHz, tetramethylsilane as an internal standard). ^{11}B-NMR spectra were recorded in CDCl$_3$ on a JEOL JNM-JX-400 instrument (BF$_3$OEt$_2$ as an external standard). IR spectra were obtained on a Perkin Elmer 1600 spectrometer. Gel permeation chromatographic analyses were carried out on a Tosoh HLC-8020 (TSK gel G3000, G4000, or Shodex AC804) by using THF as an eluent after calibration with standard polystyrene samples. Thermogravimetric analysis (TGA) was made on a Shimadzu DT-30 instrument (15°C/min.) under air or nitrogen stream. Differential scanning calorimetry (DSC) was measured on a Seiko DSC200 instrument (10°C/min.).

Synthesis of 3a from 1 and 2a. To a nitrogen-replaced two-necked flask equipped with a septum inlet and a three-way cock, **2a** (0.064g, 0.50mmol) and **1** (0.137g, 1.02mmol, 1.02eq.) were added at 0°C under nitrogen. After 3h at ambient temperature, the glassy reaction product thus obtained was dissolved in 2ml of THF and reprecipitated into 30ml of EtOH/H_2O (v/v=1/1). The obtained polymer was freeze-dried with benzene. Yield; 0.154g (78%). All the spectroscopic data of **3a** are given in Results and Discussion. In a similar manner, **3b**-**3h** were obtained. **3b** (from 0.060g (0.47mmol) of **2b** and 0.123g (0.92mmol) of **1**): Yield 0.164g (89%); ^{1}H-NMR (δ, ppm) 0.72-2.13 ($B-CH_2-C=C$, 8H), 3.43 ($N=C-CH_2-C=C$, m 4H), 4.20-6.68 ($-CH=CH_2$, 18H), 6.95-7.66 (C_6H_4, 4H); IR (neat) 3066, 2965, 2912, 1660, 1632, 1505, 1463, 1423, 1399, 1292, 1196, 1094, 1017, 995, 970, 920, 891cm^{-1}. **3c** (from 0.031g (0.39mmol) of **2c** and 0.107g (0.80mmol) of **1**): Yield 0.106g (71%); ^{1}H-NMR (δ, ppm) 1.22-1.97 ($B-CH_2-C=C$, 8H), 2.54 ($-CH_2CH_2-C=N$, br 4H), 3.15 ($N=C-CH_2-C=C$, m 4H), 4.41-6.52 ($-CH=CH_2$, 18H); IR (neat) 3067, 2965, 2908, 1667, 1652, 1634, 1428, 1402, 1295, 1202, 1083, 997, 920, 834cm^{-1}. **3d** (from 0.047g (0.50mmol) of **2d** and 0.129g (0.96mmol) of **1**): Yield 0.140g (78%); ^{1}H-NMR (δ, ppm) 1.20-1.99 ($B-CH_2-C=C$, $-C-CH_2-C-$, 10H), 2.25 ($-C-CH_2-C=N$, br 4H), 3.13 ($N=C-CH_2-C=C$, m 4H), 4.56-6.42 ($-CH=CH_2$, 18H); IR (neat) 3066, 2966, 2907, 1668, 1634, 1458, 1424, 1400, 1297, 1201, 1086, 995, 922, 891cm^{-1}. **3e** (from 0.058g (0.53mmol) of **2e** and 0.143g (1.07mmol) of **1**): Yield 0.162g (81%); ^{1}H-NMR (δ, ppm) 1.18-1.90 ($B-CH_2-C=C$, $-C-CH_2-C-$, 12H), 2.29 ($-C-CH_2-C=N$, br 4H), 3.11 ($N=C-CH_2-C=C$, m 4H), 4.59-6.30 ($-CH=CH_2$, 18H); IR (neat) 3067, 2966, 2907, 1666, 1634, 1425, 1400, 1293, 1263, 1201, 1086, 995, 921, 890cm^{-1}. **3f** (from 0.057g (0.47mmol) of **2f** and 0.128g (0.96mmol) of **1**): Yield 0.169g (93%); ^{1}H-NMR (δ, ppm) 1.18-1.86 (B-CH$_2$-C=C, -C-CH$_2$-C-, 14H), 2.29 (-C-CH$_2$-C=N, br 4H), 3.11 (N=C-CH$_2$-C=C, m 4H), 4.50-6.38 (-CH=CH$_2$, 18H); IR (neat) 3067, 2966, 2908, 1668, 1634, 1458, 1425, 1400, 1299, 1270, 1201, 1086, 995, 920, 889cm^{-1}. **3g** (from 0.076.g (0.56mmol) of **2g** and 0.148g (1.10mmol) of **1**): Yield 0.192g (85%); ^{1}H-NMR (δ, ppm) 1.06-2.05 (B-CH$_2$-C=C, -C-CH$_2$-C-, 16H), 2.27 (-C-CH$_2$-C=N, br 4H), 3.12 (N=C-CH$_2$-C=C, m 4H), 4.42-6.37 (-CH=CH$_2$, 18H); IR (neat) 3067, 2966, 2933, 1667, 1634, 1461, 1425, 1400, 1296, 1267, 1201, 1086, 995, 920, 889cm^{-1}. **3h** (from 0.082g (0.50mmol) of **2h** and 0.133g (0.99mmol) of **1**): Yield 0.191g (89%); ^{1}H-NMR (δ, ppm) 1.02-1.98 (B-CH$_2$-C=C, -C-CH$_2$-C-, 18H), 2.27 (-C-CH$_2$-C=N, br 4H), 3.11 (N=C-CH$_2$-C=C, m 4H), 4.47-6.32 (-CH=CH$_2$, 18H); IR (neat) 3067, 2966, 2929, 2856, 1666, 1634, 1464, 1425, 1400, 1298, 1269, 1201, 1086, 995, 920, 888, 678cm^{-1}.

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2) (a) Paine, R. T.; Narula, C. K. *Chem. Rev.*, **1990**, 90, 73.
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3) (a) See Chapter4, Sections 1-2 (b) See Chapter4, Sections 3-4.

4) (a) Bubnov, Yu. N.; Mikhailov, B. M. *Izv. Akad. Nauk SSSR, Ser. Khim.*, **1967**, 472. (b) Bubnov, Yu. N.; Bogdanov, V. S.; Mikhailov, B. M. *Zh. Obsh. Khim.*, **1968**, 38, 260.

5) Bubnov, Yu. N.; Tsyban', A. V.; Mikhailov, B. M. *Izv. Akad. Nauk SSSR, Ser. Khim.*, **1976**, 2842.

6) The IR spectrum of this liquid (after the reaction for 5min.) indicated almost complete conversion of nitrile groups. The formation of monomeric iminoborane species was supported by

the peak at 1814cm^{-1}, which was converted gradually to the dimeric iminoboranes (1659cm^{-1}) after the longer reaction time.

7) Monomeric iminoboranes show their absorptions around 30-35ppm. See, for example, (a) Mikhailov, B. M.; Ter-Sarkisyan, G. S.; Govorov, N. N.; Nikolaeva, N. A. *Izv. Akad. Nauk SSSR, Ser. Khim.*, **1976**, 1820. (b) Mikhailov, B. M.; Ter-Sarkisyan, G. S.; Govorov, N. N. *Izv. Akad. Nauk SSSR, Ser. Khim.*, **1976**, 1823.

8) IR (KBr) 3596, 3040, 2998, 2920, 1636, 1472, 1391, 998, 918, 717cm^{-1}.

9) (a) Mikhailov, B. M.; Tutorskaya, F. B. *Dokl. Akad. Nauk SSSR*, **1958**, 123, 480. (b) Brown, H. C.; Racherla, U. S. *J. Org. Chem.*, **1986**, 51, 427.

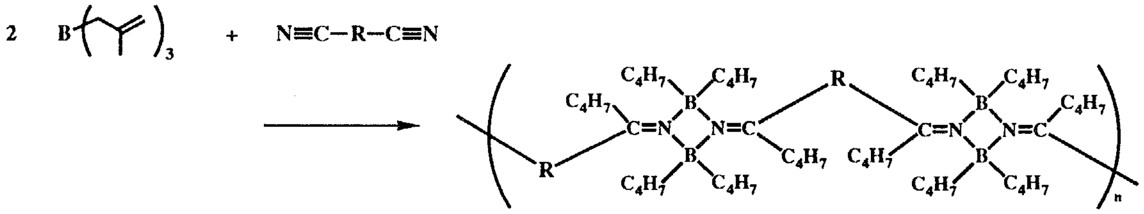
5 - 2

Synthesis of Boron-Containing Polymers by the Reaction between Trimethallylborane and Dicyano Compounds.

Introduction

In Section 1, the author has described "Allylboration Polymerization" of dicyano monomers with triallylborane to produce the corresponding boron-containing polymers in high yields. The obtained polymers were, however, rather unstable upon the storage under nitrogen as well as under air to be crosslinked. These polymers might be attractive for the precursors of inorganic boron-containing materials by the pyrolysis or for the materials having interesting properties. As to know the polymerizability of borane monomers for the present method as well as the properties of the obtained polymers by changing the structures of borane monomers, trimethallylborane was applied to the present allylboration polymerization (Scheme I).

Scheme I



Results and Discussion

First of all, the polymerization between trimethallylborane (**1**) and adiponitrile (**2c**) was examined to clarify the polymerization behavior. When 2 molar equivalents of **1** was added to **2c** in bulk at ambient temperature, two monomers dissolved each other to form a colorless solution, which became viscous after several hours. From the results of gas chromatographic analysis, the conversion of **2c** was found to be completed within a minute. However, the molecular weight in GPC was found to be increased very slowly (Figure 1).

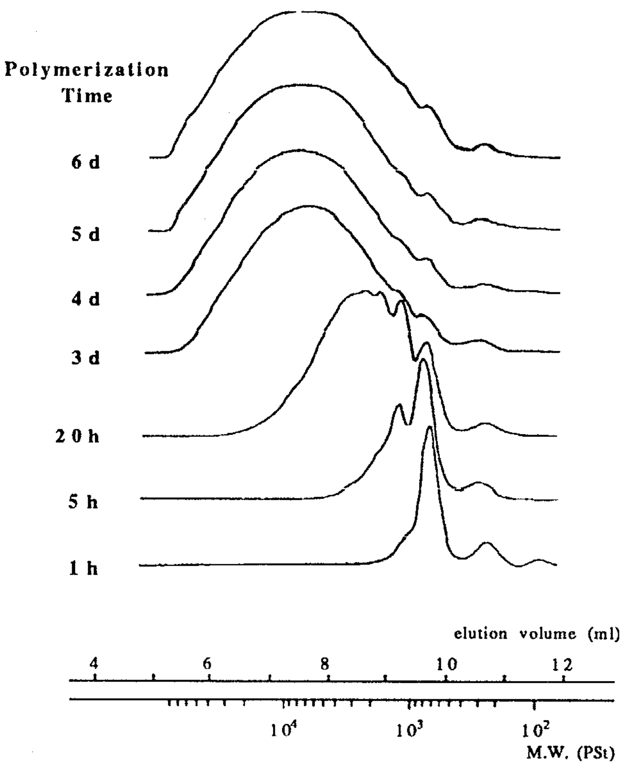


Figure 1 GPC traces of the products obtained from 1 and 2c by changing the polymerization time.

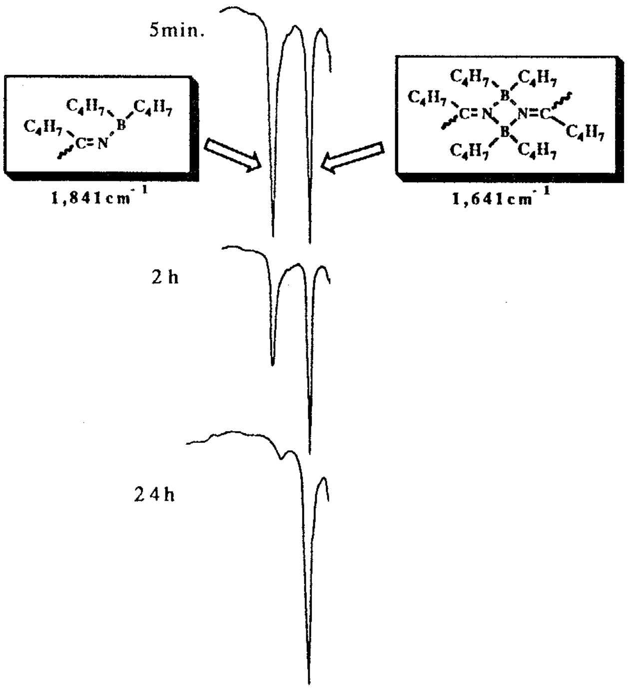
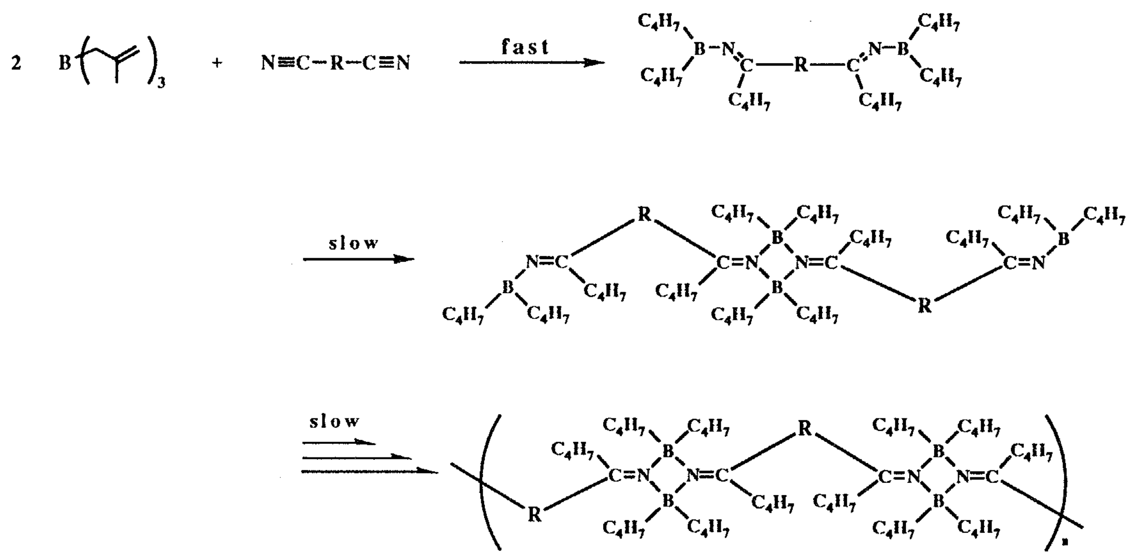


Figure 2 IR spectra of the products obtained from 1 and 2c after 5min., 2h, and 24h.

In the IR spectrum after the reaction for 5 min., the nitrile group was completely disappeared and specific peaks at 1,841 and 1641cm^{-1} were observed (Figure 2). The former peak can be attributed to the monomeric iminoborane and the latter to the dimeric one[1]). After the reaction for 2 h, the peak at 1841cm^{-1} became smaller and the corresponding peak almost disappeared after the reaction for 1 day[2]). Accordingly, it can be concluded that the present polymerization consists of two stepwise reactions, i.e., the fast allylboration reaction to form a monomeric iminoborane and the slow dimerization of the iminoborane to form poly(cyclodiborazane) (Scheme II).

Scheme II



The structure of the polymer (**3c**) obtained after the reaction for 3 days was confirmed by ^{1}H-NMR and IR spectra. In its ^{1}H-NMR spectrum (Figure 3), the peak assignable to the methylene adjacent to boron, methyl on vinyl group, and inner methylenes, the peak assignable to methylenes adjacent to imine, the peak assignable to methylenes between vinyl and imine, and the peak assignable to the vinyl protons were observed at 1.04-2.01, 2.35, 3.19, and 4.23-5.16 ppm, respectively. The integral ratios of these peaks were in good agreement to those for the expected structure.

In the IR spectrum of **3c**, as discussed above, no nitrile group was detected and a strong peak at 1,640cm^{-1} attributable to dimeric iminoborane was observed (Figure 4).

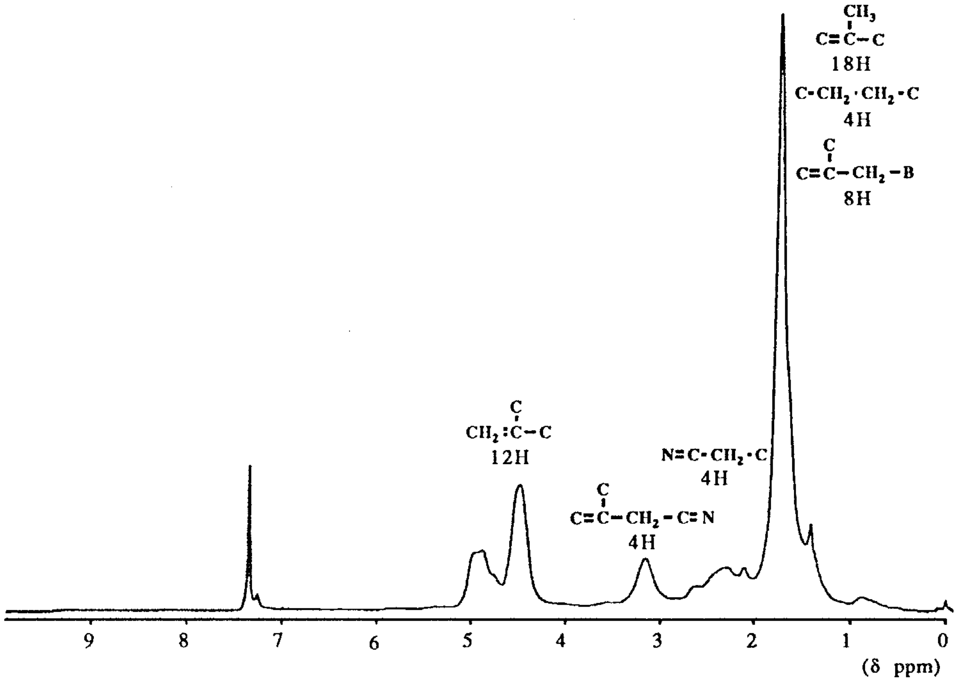


Figure 3 ^{1}H-NMR spectrum of 3c.

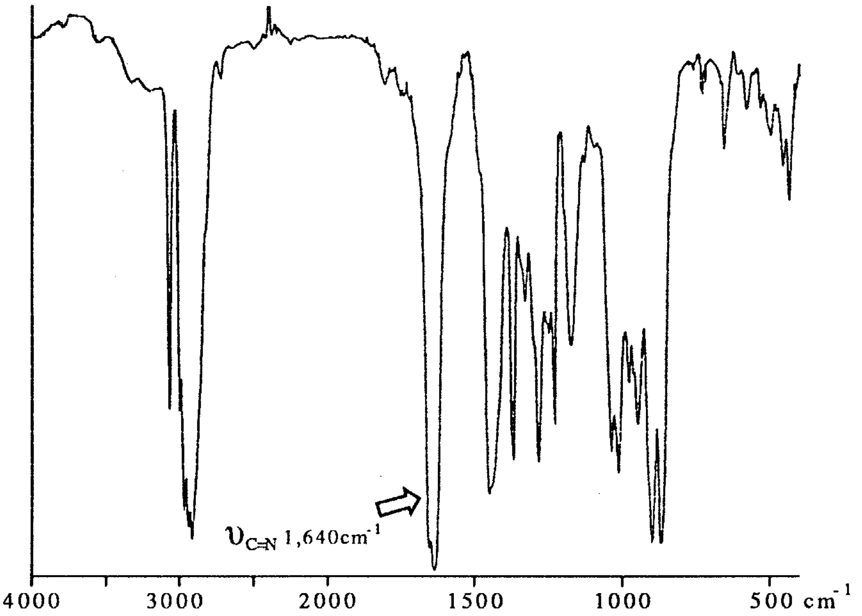


Figure 4 IR spectrum of 3c.

The results of allylboration polymerization between **1** and various dicyano monomers (**2a**-**2g**) are summarized in Table I. α,ω-Dicyanoalkanes having longer than three methylenes (**2b**-**2f**) produced the boron-containing polymers in high yields. In the case of succinonitrile (**2a**), however, only oligomers were obtained.

In the case of triallylborane, polymerization with **2a** produced a boron-containing polymer similarly to **2b**-**2f**3). In the IR spectrum of the oligomer obtained from **1** and **2a**, the complete conversion of nitrile group was observed. Therefore, it seems that insufficient polymerizability of **2a** was caused by the insufficient dimerization of the iminoborane due to the steric repulsion between the adjacent units. Similarly to this, **2g** gave only oligomers even after the reaction for 6 days due to the insufficient dimerization of the iminoboranes, which was observed in its IR spectrum. All the polymers (**3b**-**3f**) obtained from **2b**-**2f** were found to have the expected structures which were confirmed by their ^{1}H-NMR and IR spectra.

Table I Allylboration Polymerization of Various Dicyano Compounds (2a-2g) with 1a)

Run	Dicyano Compounds	Yieldb) (%)	M_nc)	M_wc)
1	$NC(CH_2)_2CN$ (2a)	n.d.d)	650	940
2	$NC(CH_2)_3CN$ (2b)	93	2,880	5,280
3	$NC(CH_2)_4CN$ (2c)	91	5,430	10,600
4	$NC(CH_2)_5CN$ (2d)	93	4,340	7,990
5	$NC(CH_2)_6CN$ (2e)	87	3,700	6,580
6	$NC(CH_2)_8CN$ (2f)	84	3,750	8,300
7	m-NCC_6H_4CN (2g)	n.d.d)	1,030	1,350

a) Polymerizations were carried out in bulk for 6 days.
b) Isolated yields after precipitation into $EtOH/H_2O$ (v/v=1/1).
c) GPC (THF), Polystyrene standard.
d) Not determined.

The air-stability of **3c** was checked by monitoring the change of its molecular weight after keeping the sample under air (Figure 5). Although the polymer from **1** was somewhat stable under air in comparison with that from triallylborane, it was found to be gradually decomposed to the lower molecular weight oligomers.

In comparison with triallylborane, **1** was found to require much longer reaction time for the complete polymerization (i.e., dimerization of monomeric iminoborane species). As the insufficient stability of the polymers obtained from triallylborane or **1** seems to be originated from the residual allyl moieties on the boron atom, monomers having only one allyl group on each boron atom can be expected to resolve this problem, which will be described in the following section.

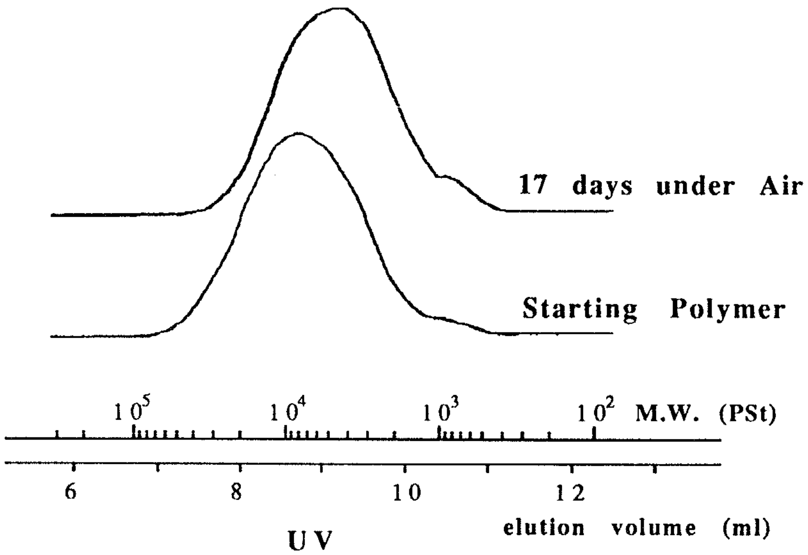


Figure 5 GPC traces of 3c (just after preparation) and the product kept under air for 17 days.

Experimental Section

Materials and Instruments. Ethanol and benzene were used as received. **1** was prepared as reported earlier4), and purified by distillation under nitrogen. **2a** was purified by sublimation. **2b**-**2f** were purified by distillation under reduced pressure. **2g** was recrystallized from ethyl acetate.

^{1}H-NMR spectra were recorded in $CDCl_3$ on a Hitachi R-600 instrument (60MHz, tetramethylsilane as an internal standard). IR spectra were obtained on a Perkin Elmer 1600 spectrometer. Gas chromatographic analyses were made on a Simadzu GC-6A instrument. Gel permeation chromatographic analyses were carried out on a Tosoh HLC-8020 (TSK gel G3000) by using THF as an eluent after calibration with standard polystyrene samples.

Synthesis of 3c from 1 and 2c. To a two-necked flask equipped with a septum inlet and a three-way cock, **2c** (0.0899g, 0.83mmol) and **1** (0.291g, 1.65mmol) were added at 0°C under nitrogen. After stirring the reaction mixture at ambient temperature for 6 days, the viscous reaction product was dissolved into 2ml of THF and was precipitated with EtOH/H_2O (v/v=1/1). **3c**: Yield 0.348g (91%); ^{1}H-NMR (δ, ppm) 1.04-2.01 (B-CH_2-C=C, -C-CH_2-C-, C=C-CH_3, total 30H), 2.35 (-C-CH_2-C=N, br 4H), 3.19 (N=C-CH_2-C=C, m 4H), 4.23-5.16 (-C=CH_2, 12H); IR (neat) 3072, 2971, 2942, 2915, 1805 (w), 1640, 1451, 1371, 1285, 1229, 1175, 1015, 902, 872cm^{-1}.

When the reaction mixture was subjected to GPC measurements directly after the reaction for 1h, 5h, 20h, 3 days, 4 days, 5 days, and 6 days, the molecular weight of **3c** was found to increase rather slowly and the polymerization was completed within a few days (see Figure 1). Thus, polymerizations of other dicyano monomers were carried out for 6 days. **3a** (from 0.074g (0.92mmol) of **2a** and 0.323g (1.83mmol) of **1**): (without isolation). **3b** (from 0.079g (0.84mmol) of **2b** and 0.287g (1.63mmol) of **1**): Yield 0.352g (93%); ^{1}H-NMR (δ, ppm) 1.16-1.98 (B-CH_2-C=C, -C-CH_2-C-, C=C-CH_3, total 28H), 2.35 (-C-CH_2-C=N, br 4H), 3.15 (N=C-CH_2-C=C, m 4H), 4.29-5.13 (-C=CH_2, 12H); IR (neat) 3072, 2915, 1806 (w), 1638, 1446, 1374, 1285, 1174, 1015, 904, 873cm^{-1}. **3d** (from 0.103g (0.84mmol) of **2d** and 0.299g (1.70mmol) of **1**): Yield 0.370g (93%); ^{1}H-NMR (δ, ppm) 0.98-2.03 (B-CH_2-C=C, -C-CH_2-C-, C=C-CH_3, total 32H), 2.27 (-C-CH_2-C=N, br 4H), 3.19 (N=C-CH_2-C=C, m 4H), 4.21-5.22 (-C=CH_2, 12H); IR (neat) 3072, 2940, 2916, 1807 (w), 1640, 1450, 1370, 1283, 1231, 1173, 1039, 1015, 908, 873cm^{-1}. **3e** (from 0.122g (0.90mmol) of **2e** and 0.311g (1.76mmol) of **1**): Yield 0.381g (87%); ^{1}H-NMR (δ, ppm) 1.04-2.03 (B-CH_2-C=C, -C-CH_2-C-, C=C-CH_3, total 34H), 2.31 (-C-CH_2-C=N, br 4H), 3.19 (N=C-CH_2-C=C, m 4H), 4.25-5.20 (-C=CH_2, 12H); IR (neat) 3072, 2940, 1805 (w), 1641, 1450, 1371, 1285, 1231, 1173, 1015, 901, 872cm^{-1}. **3f** (from 0.141g (0.86mmol) of **2f** and 0.285g (1.62mmol) of **1**): Yield 0.376g (84%); ^{1}H-NMR (δ, ppm) 1.00-1.99 (B-CH_2-C=C, -C-CH_2-C-, C=C-CH_3, total 38H), 2.29 (-C-CH_2-C=N, br 4H), 3.17 (N=C-CH_2-C=C, m 4H), 4.21-5.09 (-C=CH_2, 12H); IR (neat) 3072, 2931, 1638, 1452, 1374, 1284, 1173, 1015, 901, 872cm^{-1}.

Synthesis of 3g from 1 and 2g. To a two-necked flask equipped with septum inlet and three-way cock, **2g** (0.059g, 0.46mmol) and **1** (0.177g, 1.00mmol) were added at 0°C under nitrogen. After stirring the reaction mixture at ambient temperature, the viscous reaction product was subjected to GPC measurement, from which the formation of an oligomer was detected after the reaction for 6 days. **3g** (without isolation); IR (neat) 3397, 3072, 2967, 1812, 1641, 1480, 1344, 893cm^{-1}.

References and Notes

1) The former peak can be attributed to the monomeric iminoborane and the latter to the dimeric iminoborane. See, for example, (a) Mikhailov, B. M.; Ter-Sarkisyan, G. S.; Govorov, N. N.; Nikolaeva, N. A. *Izv. Akad. Nauk SSSR, Ser. Khim.*, **1976**, 1820. (b) Mikhailov, B. M.; Ter-Sarkisyan, G. S.; Govorov, N. N. *Izv. Akad. Nauk SSSR, Ser. Khim.*, **1976**, 1823.
2) In the case of the polymerization in chloroform (1.0M), the monomeric form was still predominant even after the reaction for 1 day. Thus, the slow dimerization process could be concluded to require higher reaction concentration.
3) See 5-1.
4) (a) Mikhailov, B. M.; Tutorskaya, F. B. *Dokl. Akad. Nauk SSSR*, **1958**, 123, 480. (b) Brown, H. C.; Racherla, U. S. *J. Org. Chem.*, **1986**, 51, 427.

5 - 3

Synthesis of Boron-Containing Polymers by the Reaction between Allyldialkylboranes and Dicyano Compounds.

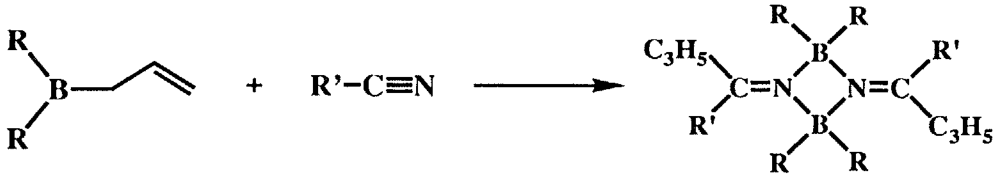
Introduction

In Sections 1 and 2, the author has described a new methodology to obtain the boron-containing polymers having cyclodiborazane backbones *via* allylboration reaction of dicyano monomers with triallylborane or trimethallylborane, respectively. The polymers obtained in these systems were found to be rather unstable upon the storage presumably due to the allyl substituents on the boron atom remaining in the polymer structures. As only one allyl group on the borane monomer participates in the allylboration reaction in the present polymerization system, the derivatives of monoallylborane can be also utilized for the polymerization reaction. The stability of the polymers produced from allyldialkylboranes should be improved since the boron atoms in these polymers have no more allyl groups. Thus, in the present section, allylboration polymerizations of dicyano monomers with allyldialkylboranes are described.

Results and Discussion

According to the previous report by Mikhailov *et al.*, derivatives of cyclodiborazanes (i.e., iminoborane dimers) have been obtained quantitatively by the allylboration reaction of allyldialkylboranes towards nitriles such as acetonitrile and benzonitrile1) followed by the dimerization (Scheme I). Accordingly, the reaction of allyldialkylboranes with bifunctional dicyano monomers may produce the corresponding boron-containing polymers bearing boron-nitrogen four-membered rings in the main chain, similarly to the case of triallylborane2) or trimethallylborane3).

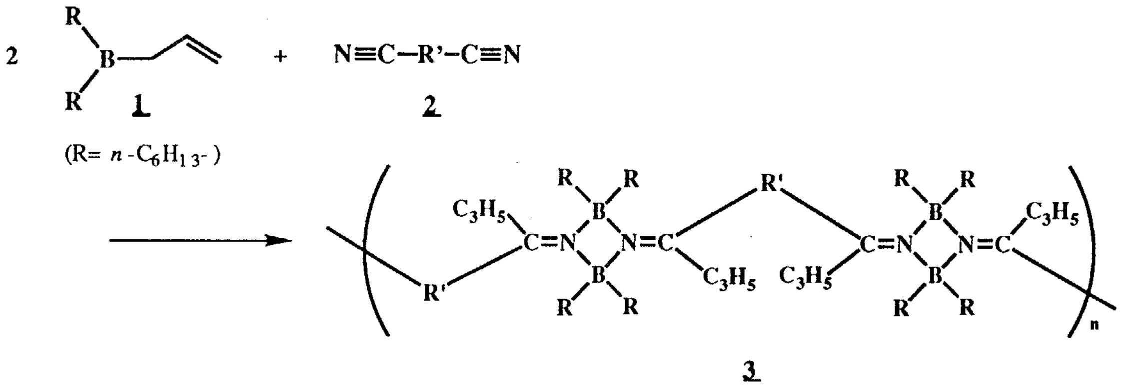
Scheme I



R= -Et, -Pr-*n*, -Bu-*n* R'= -Me, -Ph

First, allyldi-*n*-hexylborane (**1**) was used as a borane monomer and polymerizations were carried out with dicyano compounds (**2a**-**2e**) (Scheme II). In the case of adiponitrile (**2b**), the polymerization proceeded by a two-phase system at the early stage of the reaction, which turned to a homogeneous colorless liquid and gradually became viscous. The molecular weight of the resulting polymer in GPC showed no significant change after the reaction for several hours. When the obtained colorless gum was dissolved in THF and was precipitated into ethanol/water (v/v=1/1), the boron-containing polymer (**3b**) was isolated in 72% yield. The structure of **3b** was confirmed by its ^{11}B-, ^{1}H-NMR, and IR spectra. In the ^{11}B-NMR spectrum, a peak at 4.5ppm attributable to the cyclodiborazane structure and small peaks presumably owing to the monomeric iminoborane and some impurities were observed at 33 and 55ppm, respectively (Figure 1).

Scheme II



In the ^{1}H-NMR spectrum of **3b** (Figure 2), olefinic protons in the allyl group, methylenes between the imine and the double bond (i.e., methylenes of the allyl group), methylenes adjacent to the imine (i.e., methylenes in the main chain), and other protons (i.e., inner methylenes and *n*-hexyl group on the boron atom) were observed at 4.81-6.49, 3.07, 2.29, and 0.31-1.04ppm, respectively.

The observed integral ratios of these peaks (7.6:3.3:5.3:56) were in good agreement with the calculated values for the expected structure (6:4:4:56).

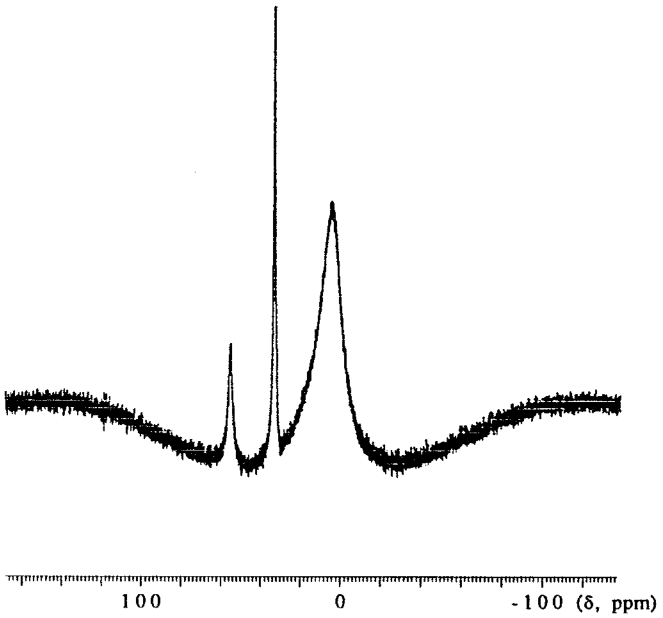


Figure 1 ^{11}B-NMR spectrum of 3b.

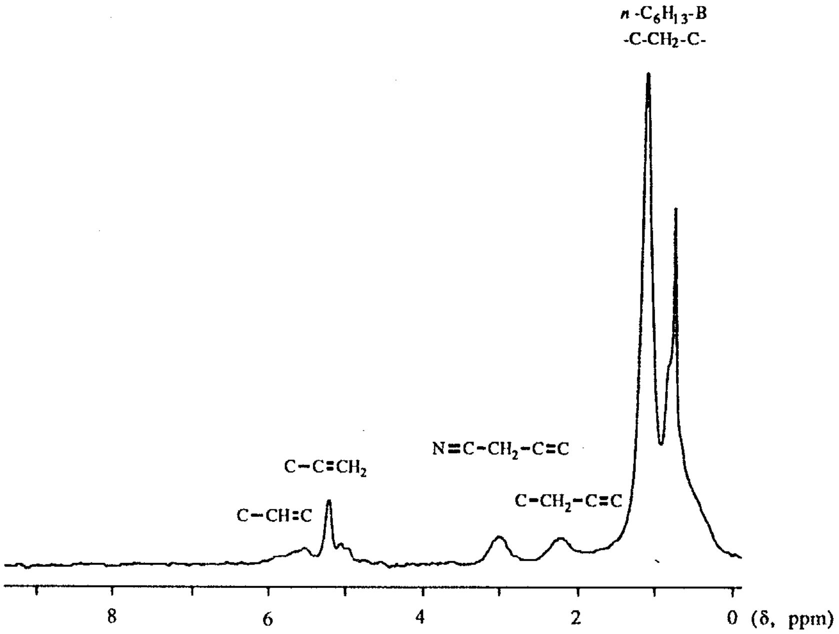


Figure 2 ^{1}H-NMR spectrum of 3b.

In the IR spectrum of 3b (Figure 3), the nitrile groups were completely consumed and a characteristic absorption band at 1,666cm^{-1} attributable to the dimeric iminoborane was observed. Though the intensity of a peak around 1800cm^{-1} was very small, this peak indicates that monomeric iminoboranes may be present at the end of the polymer chains.

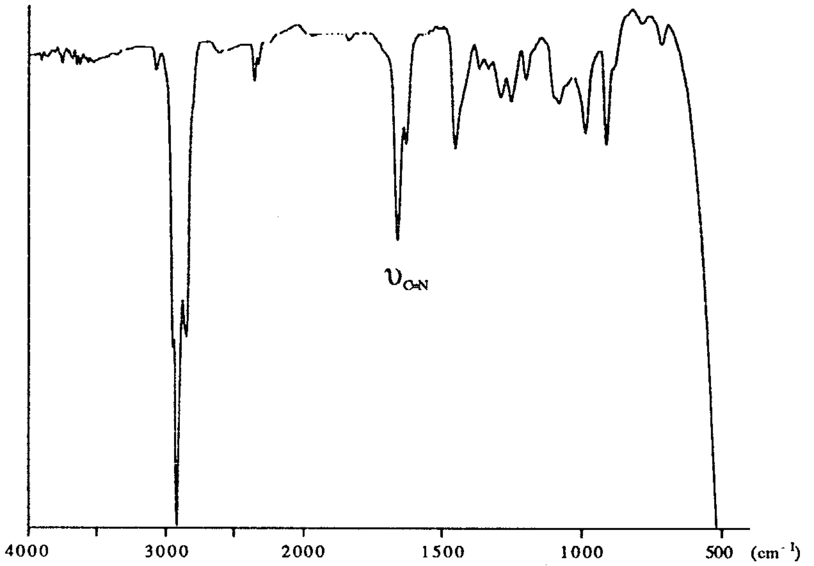


Figure 3 IR spectrum of 3b.

Table I Allylboration Polymerization of Various Dicyano Compounds (2a-2e) with 1[a].

Run	Dicyano Compounds	Yield[b] (%)	$\overline{M}_n$[c]	$\overline{M}_w$[c]
1	NC(CH$_2$)$_3$CN (2a)	77	15,400	44,600
2	NC(CH$_2$)$_4$CN (2b)	72	27,300	103,000
3	NC(CH$_2$)$_5$CN (2c)	57	15,300	53,100
4	NC(CH$_2$)$_6$CN (2d)	76	19,200	58,800
5	NC(CH$_2$)$_8$CN (2e)	65	15,800	38,800

a) Polymerizations were carried out in bulk at 0°C.
b) Isolated yields after reprecipitation into EtOH/H$_2$O (1/1).
c) GPC (THF), polystyrene standard.

The results of allylboration polymerization of **1** with various dicyano monomers (2a-2e) are summarized in Table I. In all cases, polymerization reactions proceeded at ambient temperature to give the corresponding polymers (3a-3e) in good yields. Rate of polymerization seems to be quite similar to that using triallylborane as a monomer. In comparison with triallylborane, **1** gave the polymers having higher molecular weights. All the polymers (3a-

3e) were elastic materials which seem to have low glass transition temperatures (Tg). On the other hand, the polymers from triallylborane were glassy solids, though it was impossible to know the Tg value due to the decomposition during the measurement of DSC[2]. Therefore, one reason for the higher molecular weights in the case of **1** might be the difference of Tg values. That is, polymerizations using **1** can be continued further in the bulk system after forming polymers with high molecular weight because these polymers exist above their Tg value.

Similarly to the case of **1**, di-*n*-hexylmethallylborane (**4**) was found to be a good monomer for the present polymerization system. The results of allylboration polymerization of **4** with various dicyano monomers (**2a**-**2e**) are summarized in Table II. All the polymers (**5a**-**5e**) obtained here were found to have the expected structures which were confirmed by ^{1}H-NMR and IR. It was found that polymerizations were completed within several hours, similarly to the case of triallylborane[2], rather than trimethallylborane[3]. These results support the proposed mechanism for the present allylboration polymerization. That is, allylboration reaction of allylboron moiety towards nitrile group is a rapid process regardless to the structure of allyl moieties. However, dimerization process is largely influenced by its steric effect.

Table II Allylboration Polymerization of Various Dicyano Compounds (2a-2e) with 4[a].

Run	Dicyano Compounds	Yield[b] (%)	$\overline{M}_n$[c]	$\overline{M}_w$[c]
1	$NC(CH_2)_3CN$ (2a)	77	13,100	27,700
2	$NC(CH_2)_4CN$ (2b)	75	20,800	69,000
3	$NC(CH_2)_5CN$ (2c)	74	17,000	43,400
4	$NC(CH_2)_6CN$ (2d)	77	14,200	38,800
5	$NC(CH_2)_8CN$ (2e)	86	12,300	28,300

a) Polymerizations were carried out in bulk at 0°C.
b) Isolated yields after precipitation into $EtOH/H_2O$ (1/1).
c) GPC (THF), polystyrene standard.

The stability of the boron-containing polymers obtained from allyldialkylboranes is expected to be better than those from triallylborane or from trimethallylborane, since they have no allyl groups on the boron atom in the polymer chain. When differential scanning calorimetric analysis (DSC) of the polymer (**5b**) prepared from **4** and **2b** was carried out under nitrogen, no specific peaks were detected below 180°C. This result was entirely different from that of the polymer from triallylborane, in which irreversible chemical reaction was observed around 140°C2). Although the molecular weight of the sample after heating at 140 or 200°C was decreased (Figure 4), it should be noted that these samples never became insoluble in organic solvents4). This large difference should be originated from the residual substituents on the boron atom (Scheme III).

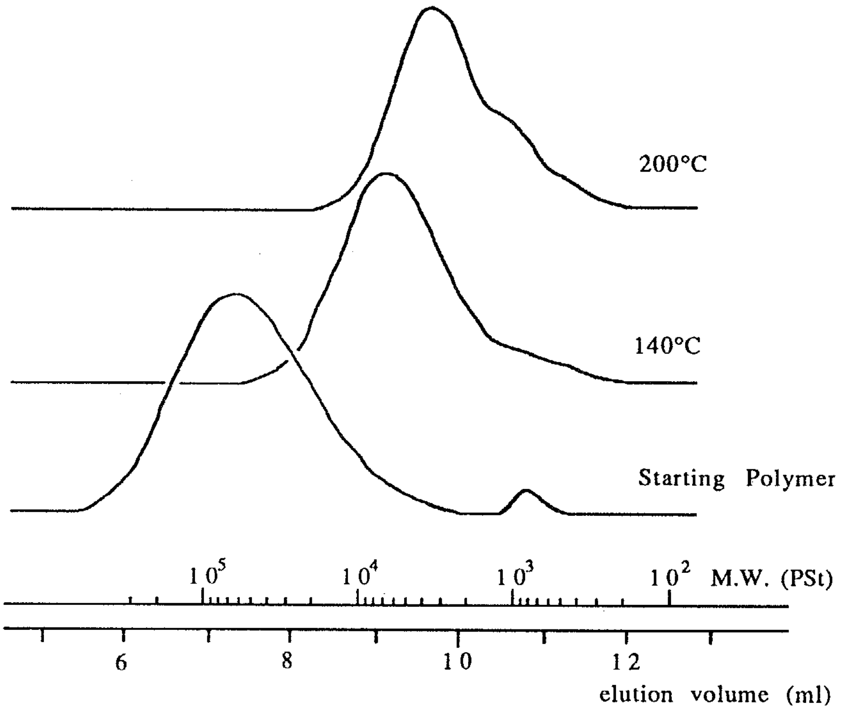
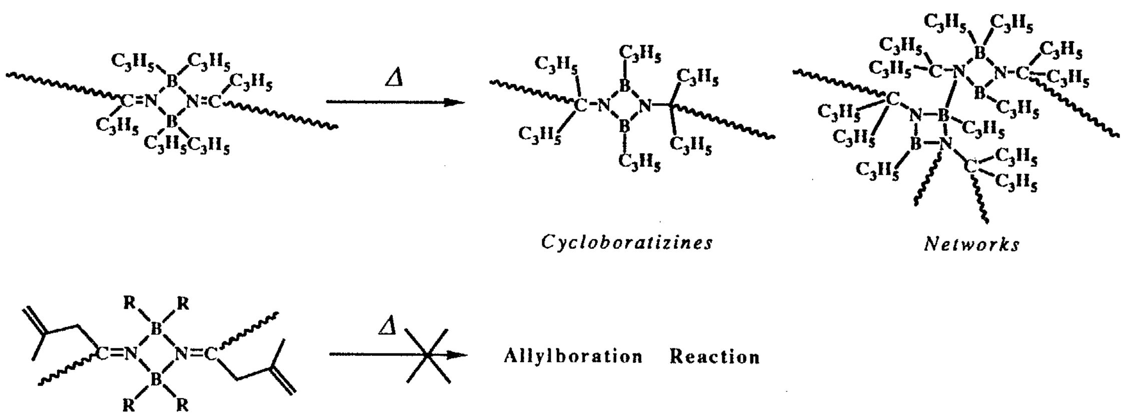


Figure 4 GPC traces of 5b , the sample heated at 140°C, and 200°C.

When the boron-containing polymer (**5b**) was kept under air for 2 months, only a small decrease in molecular weight was observed (Figure 5). This better stability in comparison with the boron-containing polymers prepared from triallylborane2) or trimethallylborane[3)] should be also due to the absence of the allyl group on the boron atom in the polymer chain.

Scheme III



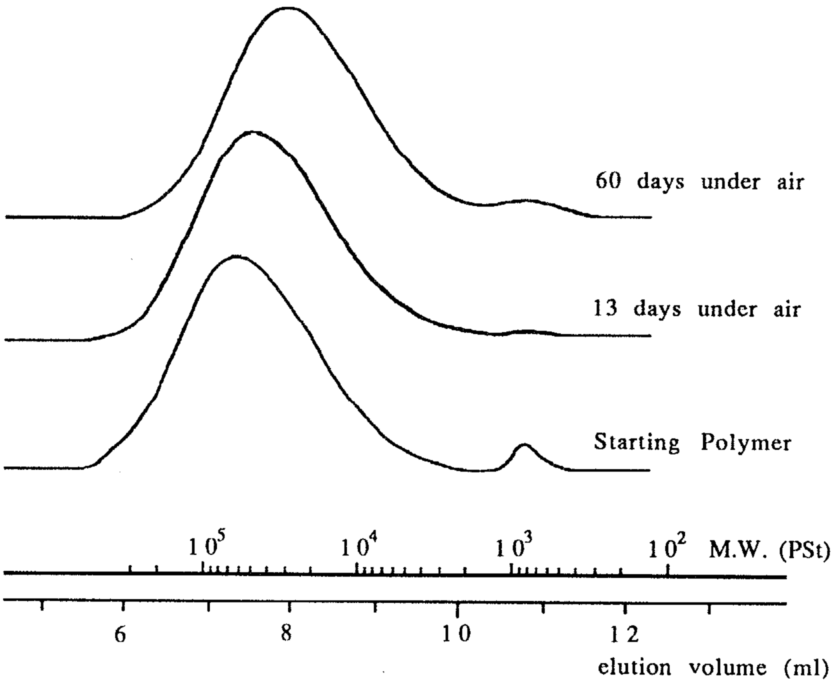


Figure 5 **GPC traces of <u>5b</u> (just after preparation), the sample kept under air for 13 days, and that kept for 2 months.**

Experimental Section

Materials and Instruments. Diethyl ether was dried over lithium aluminum hydride and distilled under nitrogen. **2a-2e**

were purified by distillation under reduced pressure. $BH_2Cl \cdot SMe_2$, 1-hexene and other reagents were used as received.

^{1}H-NMR spectra were recorded in $CDCl_3$ on a Hitachi R-600 instrument (60MHz, tetramethylsilane as an internal standard). ^{11}B-NMR spectra were recorded in $CDCl_3$ on a JEOL JNM-JX-400 instrument (128MHz, BF_3OEt_2 external standard). IR spectra were obtained on a Perkin Elmer 1600 spectrometer. Gel permeation chromatographic analyses were carried out on a Tosoh HLC-8020 (TSK gel G4000) by using THF as an eluent after calibration with standard polystyrene samples. Differential scanning calorimetry (DSC) was measured on a Seiko DSC200 instrument (10°C/min.).

Synthesis of Allyldi-*n*-hexylborane (1) and Di-*n*-hexylmethallylborane (4). The starting methyl di-*n*-hexylborinate was prepared by the reaction of 1-hexene with $BH_2Cl \cdot SMe_2$⁵⁾ followed by methanolysis and was purified by distillation. Allyldi-*n*-hexylborane (**1**) was prepared by the reaction of methyl di-*n*-hexylborinate with allylmagnesium chloride, according to the reported method for the preparation of allyldialkylboranes⁶⁾, and was purified by distillation (90-92°C/0.7mmHg). **1**: Yield 36%; ^{1}H-NMR (δ, ppm) 0.45-1.84 (n-C_6H_{13}, m, 26H), 2.13 (-CH_2-, m, 2H), 4.58-6.45 (-$CH=CH_2$, m, 3H); IR (in $CHCl_3$) 3075, 2955, 2924, 2858, 1631, 1464, 1329, 1268, 1122, 996, 902cm^{-1}.

Similarly, **4** was obtained from methyl di-*n*-hexylborinate and methallylmagnesium chloride. **4**: Yield 69%; ^{1}H-NMR (δ, ppm) 0.45-1.92 (n-C_6H_{13}, -CH_3, m, 29H), 2.06 (-CH_2-, 2H), 4.59-5.10 (-$C=CH_2$, m, 2H); IR (in $CHCl_3$) 3073, 2956, 2924, 2857, 1640, 1459, 1379, 1293, 1119, 1063, 880cm^{-1}.

Synthesis of Boron-Containing Polymers (3a-3e) from 1 and 2a-2e. As a typical example, polymerization between **1** and **2b** is shown as follows: To a nitrogen-replaced two-way flask equipped with a septum inlet and a three-way cock, **2b** (0.0469g, 0.434mmol) and **1** (0.191g, 0.857mmol) were added at 0°C, and the mixture was stirred at ambient temperature for 1 day. The resulting viscous gum was dissolved in THF and was precipitated into $EtOH/H_2O$ (v/v=1/1). After freeze-dring with benzene, **3b** was obtained in 72% yield (0.172g). The spectroscopic data are shown in Results and Discussion.

Similarly, **3a** and **3c**-**3e** were obtained by the reaction of **1** with the corresponding dicyano monomers. **3a** (from 0.0382g (0.406mmol) of **2a** and 0.207g (0.932mmol) of **1**): Yield 0.167g (77%); ^{1}H-NMR (δ, ppm) 0.22-1.92 (n-C_6H_{13}, -C-CH_2-C-, 54H), 2.34 (-C-CH_2-C=N, m, 4H), 3.07 (N=C-CH_2-C=C, m, 4H), 4.93-6.24 (-CH=CH_2, m, 6H); IR (neat) 3079, 2954, 2920, 2856, 1844 (w), 1666, 1636, 1298, 1261, 1205, 1089, 994, 920cm^{-1}. **3c** (from 0.0568g (0.465mmol) of **2c** and 0.215g (0.966mmol) of **1**): Yield 0.150g (57%); ^{1}H-NMR (δ, ppm) 0.20-1.94 (n-C_6H_{13}, -C-CH_2-C-, 58H), 2.25 (-C-CH_2-C=N, m, 4H), 3.07 (N=C-CH_2-C=C, m, 4H), 4.87-6.30 (-CH=CH_2, m, 6H); IR (neat) 3079, 2920, 2856, 1842 (w), 1666, 1637, 1459, 1296, 1263, 1206, 1105, 1089, 994, 919cm^{-1}. **3d** (from 0.0505g (0.371mmol) of **2d** and 0.169g (0.762mmol) of **1**): Yield 0.163g (76%); ^{1}H-NMR (δ, ppm) 0.22-1.80 (n-C_6H_{13}, -C-CH_2-C-, 60H), 2.25 (-C-CH_2-C=N, m, 4H), 3.05 (N=C-CH_2-C=C, m, 4H), 4.81-6.20 (-CH=CH_2, m, 6H); IR (neat) 3079, 2921, 2856, 1665, 1636, 1459, 1295, 1263, 1086, 994, 918cm^{-1}. **3e** (from 0.0629g (0.383mmol) of **2e** and 0.169g (0.760mmol) of **1**): Yield 0.158g (65%); ^{1}H-NMR (δ, ppm) 0.24-1.80 (n-C_6H_{13}, -C-CH_2-C-, 64H), 2.23 (-C-CH_2-C=N, m, 4H), 3.07 (N=C-CH_2-C=C, m, 4H), 4.90-6.20 (-CH=CH_2, m, 6H); IR (neat) 3079, 2921, 2856, 1665, 1636, 1460, 1296, 1262, 1206, 1086, 994, 918cm^{-1}.

Synthesis of Boron-Containing Polymers (5a-5e) from 4 and 2a-2e. Similarly to the case of **1**, polymerizations between **4** and **2a**-**2e** were carried out in bulk at ambient temperature for 1 day. **5a** (from 0.0500g (0.531mmol) of **2a** and 0.257g (1.09mmol) of **4**): Yield 0.226g (77%); ^{1}H-NMR (δ, ppm) 0.27-1.97 (n-C_6H_{13}, -C-CH_2-C-, -CH_3, 60H), 2.21 (-C-CH_2-C=N, m, 4H), 3.03 (N=C-CH_2-C=C, m, 4H), 4.64-5.14 (-C=CH_2, m, 4H); IR (neat) 3078, 2920, 2855, 1802 (w), 1657, 1457, 1376, 1296, 1251, 1092, 1005, 897cm^{-1}. **5b** (from 0.0855g (0.791mmol) of **2b** and 0.366g (1.55mmol) of **4**): Yield 0.343g (75%); ^{1}H-NMR (δ, ppm) 0.27-1.94 (n-C_6H_{13}, -C-CH_2-C-, -CH_3, 62H), 2.21 (-C-CH_2-C=N, m, 4H), 3.03 (N=C-CH_2-C=C, m, 4H), 4.68-5.18 (-C=CH_2, m, 4H); ^{11}B-NMR (δ, ppm) 4.2, 33.1, 54.8; IR (neat) 3077, 2920, 2856, 1649, 1457, 1248, 1090, 1004, 897cm^{-1}.

5c (from 0.0474g (0.388mmol) of **2c** and 0.179g (0.757mmol) of **4**): Yield 0.171g (74%); ^{1}H-NMR (δ, ppm) 0.33-1.97 (n-C_6H_{13}, -C-CH_2-C-, -CH_3, 64H), 2.19 (-C-CH_2-C=N, m, 4H), 3.03 (N=C-CH_2-C=C, m, 4H), 4.68-5.09 (-C=CH_2, m, 4H); IR (neat) 3077, 2920, 2856, 1648, 1457, 1375, 1299, 1255, 1100, 1004, 896cm^{-1}. **5d** (from 0.0580g (0.426mmol) of **2d** and 0.206g (0.870mmol) of **4**): Yield 0.199g (77%); ^{1}H-NMR (δ, ppm) 0.22-1.94 (n-C_6H_{13}, -C-CH_2-C-, -CH_3, 66H), 2.15 (-C-CH_2-C=N, m, 4H), 3.03 (N=C-CH_2-C=C, m, 4H), 4.60-5.09 (-C=CH_2, m, 4H); IR (neat) 3077, 2922, 2857, 1798 (w), 1649, 1457, 1375, 1296, 1255, 1208, 1100, 1005, 896cm^{-1}. **5e** (from 0.0778g (0.474mmol) of **2e** and 0.228g (0.964mmol) of **4**): Yield 0.260g (86%); ^{1}H-NMR (δ, ppm) 0.27-1.92 (n-C_6H_{13}, -C-CH_2-C-, -CH_3, 70H), 2.15 (-C-CH_2-C=N, m, 4H), 3.01 (N=C-CH_2-C=C, m, 4H), 4.68-5.07 (-C=CH_2, m, 4H); IR (neat) 3077, 2921, 2856, 1797 (w), 1648, 1457, 1376, 1298, 1250, 1104, 1002, 896cm^{-1}.

References and Notes

1) Bubnov, Yu. N.; Tsyban', A. V.; Mikhailov, B. M. *Izv. Akad. Nauk SSSR, Ser. Khim.*, **1976**, 2842.
2) See 5-1.
3) See 5-2.
4) The dimeric iminoboranes are known to be dissociated to the monomeric ones by heating. The decrease in molecular weight might be partly due to this type of thermal dissociation.
5) Brown, H. C.; Ravindran, N. *J. Org. Chem.*, **1977**, 42, 2533.
6) (a) Mikhailov, B. M.; Bubnov, Yu. N.; Tsyban', A. V. *Izv. Akad. Nauk SSSR, Ser. Khim.*, **1975**, 979. (b) Mikhailov, B. M.; Bubnov, Yu. N.; Tsyban', A. V.; Bashe, K. *Izv. Akad. Nauk SSSR, Ser. Khim.*, **1978**, 1856.

5 - 4

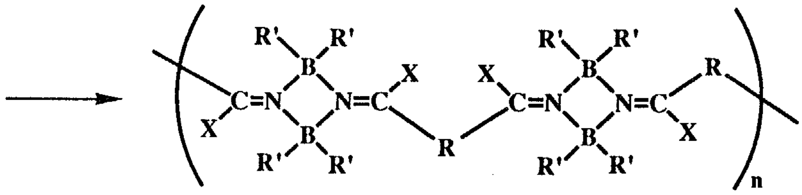
Synthesis of Boron-Containing Polymers by the Condensation Reaction between Bis(silylimine)s and Substituted Boranes.

Introduction

As described in Chapter 4 and Sections 1-3 in this chapter, stable boron-containing polymers bearing cyclodiborazane backbones (i.e., boron-nitrogen four-membered rings) were prepared by hydroboration polymerization and allylboration polymerization of dicyano compounds, respectively (Scheme I). In these systems, the substituents on the boron atoms and those on the carbon atoms of the imines were limited by the structures of the monomers used for polymerization. When condensation reactions were used to generate the iminoborane species instead of these addition reactions towards nitrile groups, a wide variety of the polymer structures may be prepared by changing the monomer structures.

Scheme I

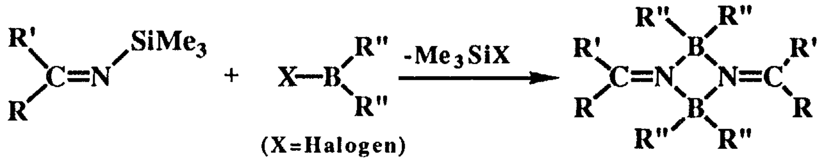
$N{\equiv}C{-}R{-}C{\equiv}N + 2\ R'_2B{-}X$



X= H, or Allyl

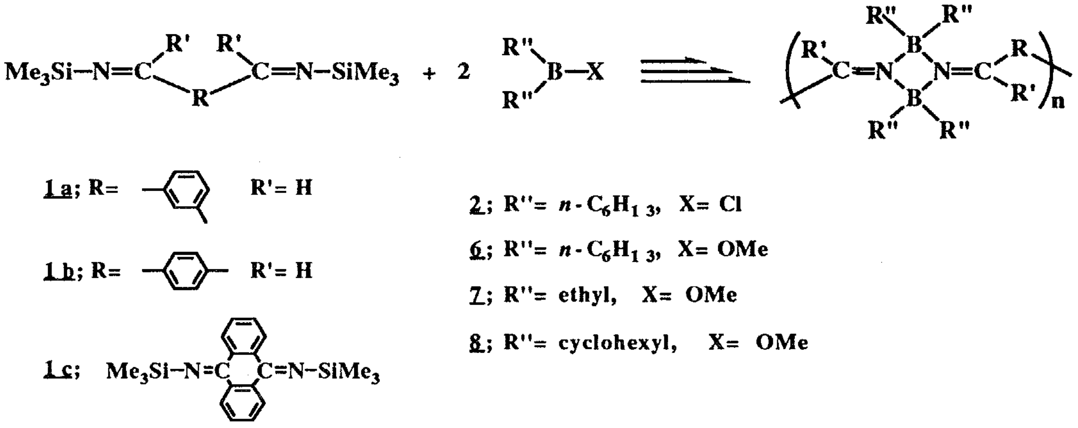
According to the previous report by Wade[1)], the reaction between *N*-silylimines and boron halides results mainly in the formation of iminoborane dimers, i.e., cyclodiborazanes (Scheme II).

Scheme II



This reaction is believed to proceed *via* the condensation between *N*-silylimine and boron halide eliminating trimethylsilyl halide followed by the dimerization. In this reaction system, various substituents on the boron atom and on the carbon atom of imine could be used. Thus, in this chapter, a novel method to prepare boron-containing polymers having cyclodiborazane backbones by the reaction using *N,N'*-bis(silylimine)s and substituted boranes was examined (Scheme III).

Scheme III



2; R''= n-C_6H_{13}, X= Cl

6; R''= n-C_6H_{13}, X= OMe

7; R''= ethyl, X= OMe

8; R''= cyclohexyl, X= OMe

Results and Discussion

The starting bis(silylimine)s (**1a**-**1c**) were prepared from the corresponding terephthalaldehyde, isophthalaldehyde, or anthraquinone, respectively, according to the reported method$^{2,3)}$. As a typical example of polycondensation, polymerization of *N,N'*-bis(trimethylsilyl)terephthalaldehyde diimine (**1a**) with monochlorodihexylborane (**2**) was examined under various reaction conditions. The polymers obtained in the present study were subjected to the GPC measurement without isolation. The results are summarized in Table I, from which the molecular weights of the resulting polymer (**3a**) showed no significant change by the solvents used (runs 1-3) nor the reaction temperature (runs 3, 4, 6). However, at the temperature of toluene-reflux, the molecular weight of **3a** was decreased by the longer reaction time in the sharp contrast to the reaction at 60°C (runs 4 and 5 vs. runs 6-8). These results may indicate that the polymers obtained by this method were rather unstable at higher temperature as described in the previous chapters4,5).

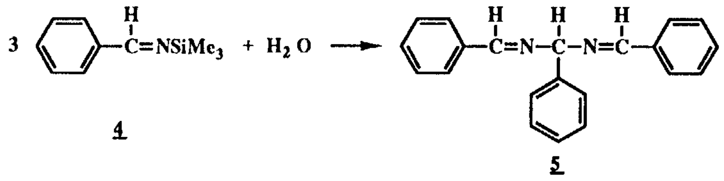
Table I Polymerization Conditionsa).

Run	**2**/**1a**	Solvent	Reaction Conditions	$\overline{M}_n$ b)	$\overline{M}_w$ b)
1	2.07	$CDCl_3$	r.t. 30min	5,800	9,000
2	2.12	CH_2Cl_2	r.t. 30min	4,500	7,100
3	2.03	toluene	r.t. 30min	5,000	7,600
4	2.20	toluene	60°C 30min	6,000	10,400
5			2h	6,000	11,500
6	2.11	toluene	reflux 15min	6,000	10,700
7			1h	4,000	5,900
8			2h	3,600	5,100

a) All the reactions were carried out in a 1.0 M solution in the solvent.
b) GPC measurement was performed without isolation.

An attempt to isolate the polymer (**3a**) by the precipitation with EtOH was not successful, because the isolated polymer (**3a**) became hardly soluble in organic solvents after keeping for several hours under air. The soluble part of the isolated polymer in hot THF was immediately subjected to GPC measurement, in which the molecular weight was found to be shifted to a higher molecular weight region in comparison with that before isolation.

Scheme V



According to the previous report, *N*-trimethylsilyl benzaldimine (**4**) is known to trimerize to form hydrobenzamide (**5**) *via* hydrolysis of *N*-trimethylsilyl group (Scheme V)$^{6)}$. Therefore, if the conversion of *N*-silylimino groups to iminoborane species was not completed, the remained *N*-silylimino groups at the polymer-end were converted to imines by protonation. Imines thus generated are considered to trimerize to form hydrobenzamide, which might yield the less soluble polymer after reprecipitation.

Due to the instability of the polymer, the characterization of **3a** was performed without isolation. ^{1}H-NMR spectra of the monomer (**1a**) and the polymer (**3a**) are shown in Figure 1. After the polymerization reaction, the chemical shift of the proton on imino carbon was shifted from 9.04ppm (*N*-silylimine) to 8.26ppm (iminoborane). The integral ratios of the peaks attributable to **3a** were in good agreement with the calculated values for the expected structure.

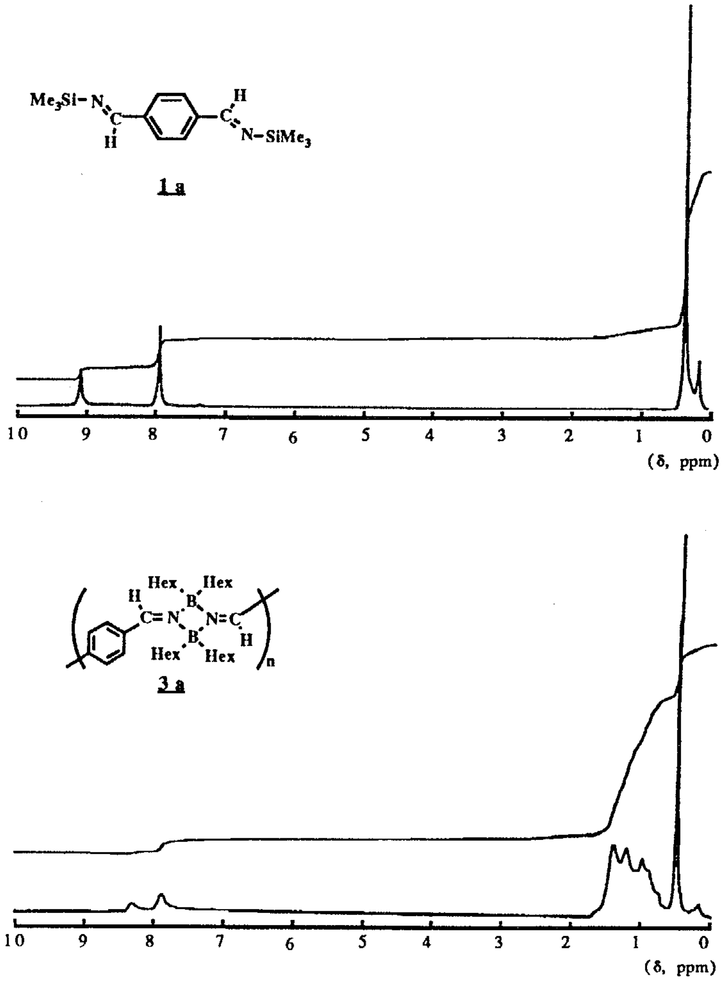


Figure 1 ^{1}H-NMR spectra of 1a and 3a.

In ^{11}B-NMR of **3a**, a broad peak around 6.2ppm was observed, which was reasonable for the four-coordinated boron-nitrogen species. In IR spectrum, the peak assignable to the dimeric iminoborane species (1644cm^{-1}) was observed.

Thermogravimetric analysis (TGA) of **3a** was measured both under air and nitrogen (Figure 2). In both cases, the black solid (about 20 wt%) was remained even after heating up to 900°C. Differential scanning calorimetry (DSC) was also measured under nitrogen (Figure 3), from which an irreversible exothermic peak was observed at the first scanning, but no peak at the second one. This may be due to some chemical reactions.

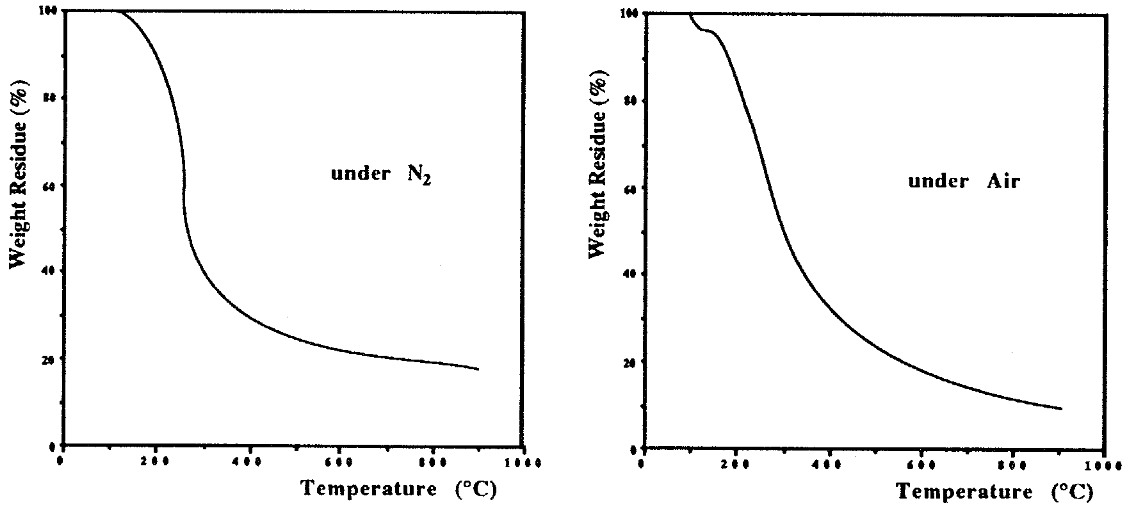


Figure 2 TGA of 3a.

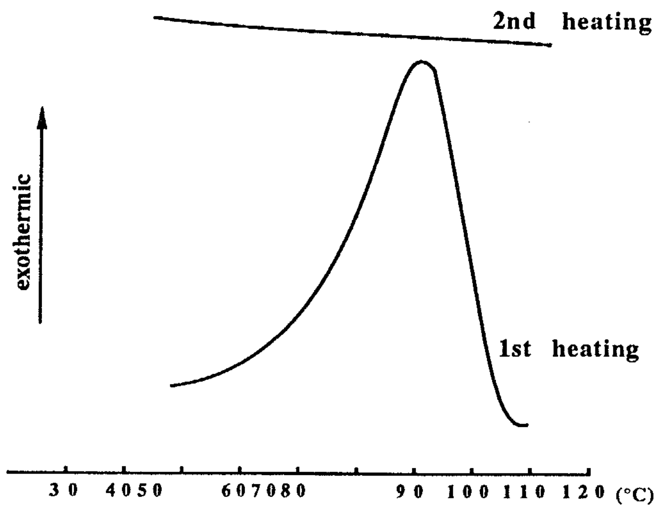
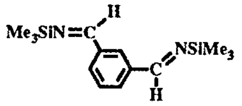
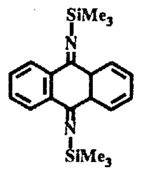


Figure 3 DSC of 3a.

Polymerization reactions using various bis(silylimine)s were examined (Table II). Similarly to the case of **1a**, *N,N'*-bis(trimethylsilyl)isophthalaldehyde diimine (**1b**) gave the corresponding polymer (**3b**), whose M_n and M_w were estimated as 6,300 and 9,620, respectively, when 2.0 eq. of **2** was used. *N,N'*-Bis(trimethylsilyl)anthraquinone diimine (**1c**), however, gave no polymer, and only monomeric iminoborane was obtained. In IR spectrum of the reaction mixture, the stretching band of C=N corresponding to monomeric iminoborane species ($1,776 cm^{-1}$) was observed. That is, **1c** was converted to monomeric iminoborane species, which, however, did not dimerize because of its sterically hindered structure.

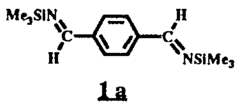
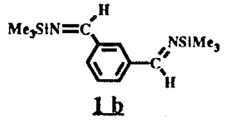
Table II Polymerization between 2 and Bis(silylimine)s (1b-c)$^{a)}$.

	Monomer		Boron-Containing Product		
Run	N,N'-Bis(silylimine)			$M_n$$^{b)}$	$M_w$$^{b)}$
1		(1b)	(3b)	6,300	9,620
2		(1c)	(3c)	no polymer	

a) polymerizations were carried out by adding small excess of 2 to a 1M $CDCl_3$ solution of *N,N'*-Bis(silylimine)s at 20°C.

b) GPC measurement was performed without isolation.

Table III Polymerization between *N,N'*-Bis(silylimine)s and Various Methyl Dialkylborinates$^{a)}$.

	Monomers			Product	
Run	N,N'-Bis(silylimine)	Methyl Dialkylborinate$^{b)}$		$M_n$$^{c)}$	$M_w$$^{c)}$
1		$MeOB(Hex)_2$ (6)	(3a)	4260	6210
2$^{d)}$		$MeOB(Et)_2$ (7)	(9a)	9000	13900
3	1a	$MeOB(CHex)_2$ (8)	(10a)	no polymer	
4		$MeOB(Hex)_2$ (6)	(3b)	4400	6570
5$^{d)}$		$MeOB(Et)_2$ (7)	(9b)	3690	5300
6	1b	$MeOB(CHex)_2$ (8)	(10b)	no polymer	

a) Polymerizations were carried out by adding small excess of methyl dialkylborinates to the 1M $CDCl_3$ solution of 1a or 1b at 20°C.

b) Hex: *n*-hexyl, Et: ethyl, CHex: cyclohexyl.

c) GPC measurement was performed without isolation.

d) Reaction was carried out in THF.

3a was found to be also prepared from **1a** and methyl dihexylborinate (**6**) instead of **2**. The results of polymerization reactions of two kinds of bis(silylimine)s (**1a** and **1b**) with some methyl dialkylborinates are summarized in Table III. Methyl diethylborinate (**7**) as well as **6** also gave the corresponding polymers from **1a** and **1b**, respectively. In the case of methyl dicyclohexylborinate (**8**), only monomeric iminoboranes (Table III, runs 3 and 6, respectively) were obtained from **1a** and **1b** due to the steric effect of cyclohexyl groups on the boron atom.

This polymerization method may provide a useful synthetic way to prepare the boron-containing polymers consisting of boron-nitrogen four-membered rings.

Experimental Section

Materials and Instruments. **2a** was prepared by the reaction of monochloroborane-dimethyl sulfide complex and 1-hexene, as reported earlier7), and was purified by distillation (90-94°C/1mmHg). **2b** was prepared by the treatment of **2a** with methanol and was purified by distillation (75-76°C/1mmHg). **2c** was prepared by the methanolysis of the readily available triethylborane using pivalic acid as a catalyst8) and was purified by distillation (45°C/760mmHg). Tetrahydrofuran and diethyl ether were dried over lithium aluminum hydride and were distilled before use. Benzene, diglyme, and toluene were dried over sodium and were distilled before use. $CDCl_3$ was dried over molecular sieves 4A. Dichloromethane was dried over P_2O_5 and distilled before use. 1,1,1,3,3,3-Hexamethyldisilazane and chlorotrimethylsilane were purified by distillation. *n*-Butyllithium (*n*-hexane solution) was obtained from Nakalai Tesque Inc., and was titrated before use.

^1H-NMR spectra were recorded in $CDCl_3$ on a Hitachi R-600 instrument. ^{11}B-NMR spectra were recorded in $CDCl_3$ on JEOL JNM-JX-400 instrument. IR spectra were obtained on a Perkin Elmer 1600 spectrometer. Gel permeation chromatographic analyses were carried out on a Tosoh HLC-8020 (TSK gel G3000, or G4000) by using THF as an eluent after calibration with standard polystyrene samples. Thermogravimetric analysis (TGA) was made on a Shimadzu DT-30 instrument (15°C/min.) under air or nitrogen stream. Differential scanning calorimetry (DSC) was measured on a Seiko DSC200 instrument (10°C/min.) under nitrogen stream.

Synthesis of Bis(silylimine)s (1a, 1b)2). To a 30ml benzene solution of $LiN(SiMe_3)_2$ (prepared from 3.87g, 24mmol of $HN(SiMe_3)_2$ and 14.2ml, 20mmol of 1.41M *n*-butyllithium in *n*-hexane)6), terephthalaldehyde (1.33g, 10mmol) in 25ml benzene was added dropwise at 50°C under nitrogen. After stirring for 3h at 70°C, chlorotrimethylsilane (2.17g, 20mmol) in 10ml benzene was added to the reaction mixture and this mixture was refluxed for 3h. The resulting mixture was cooled and then filtered to remove lithium chloride. After evaporation of the solvent, Kugelrohr distillation (130°C/1mmHg) gave 1.68g (6.1mmol, 61% yield) of **1a**. **1a**: ^{1}H-NMR (δ, ppm) 0.27 ($-SiMe_3$, s, 18H), 7.89 (C_6H_4, s, 4H), 9.06 (-CH=N-, s, 2H); IR (cell, in $CDCl_3$) 3023, 2961, 1642, 1423, 1216, 1095, 1023, 852cm^{-1}; m.p.75-82°C.

In a similar manner to **1a**, **1b** was obtained in 61% (130°C/0.85mmHg). **1b**: ^{1}H-NMR (δ, ppm) 0.27 ($-SiMe_3$, s, 18H), 7.73-8.32 (C_6H_4, 4H), 9.08 (-CH=N-, s, 2H); IR (cell, in $CDCl_3$) 2960, 2827, 1648, 1432, 1254, 1142, 1079, 852,cm^{-1}; m.p.45-48°C.

Preparation of Bis(silylimine) (1c)3). To a 50ml benzene suspension of anthraquinone (1.98g, 9.5mmol), a 26ml benzene solution of $LiN(SiMe_3)_2$ (prepared from 5.65g, 35mmol of $HN(SiMe_3)_2$ and 20ml, 28.2mmol of 1.41M *n*-butyllithium in *n*-hexane) was added slowly by a dropping funnel at 70°C under nitrogen. After refluxing for 6h, chlorotrimethylsilane (3.06g, 28.2mmol) in 10ml benzene was added slowly at that temperature. The reaction mixture was refluxed for 4h, and then cooled. This mixture was filtered to remove lithium chloride. After evaporation of the solvent, Kugelrohr distillation (150°C/0.5mmHg) gave 1.39g (4.0mmol, 42% yield) of **1c**. **1c**: ^{1}H-NMR (δ, ppm) 0.45 ($-SiMe_3$, s, 18H), 7.16-8.38 (aromatic, 8H); IR (cell, in $CDCl_3$) 2957, 1673, 1255, 1031, 938, 845cm^{-1}; m.p.100-110°C (lit.3) 118-120°C).

Synthesis of 3a from 1a and 2 (Table I, run 2). To a 1M $CDCl_3$ solution of **1a** (0.27g, 0.98mmol), **2** (0.44g, 2.0mmol) was added slowly by using a syringe at room temperature under nitrogen. After 30min. stirring at that temperature, GPC analysis was subjected directly. The spectroscopic data of **3a** are given in the part of Results and Discussion. In a similar manner, **3a** was prepared under various conditions. These results are summarized in Table I. Similarly, **3a** was also prepared from **1a** (0.14g, 0.49mmol) and **6** (0.22g, 1.0mmol) (Table III, run 1).

Synthesis of 3b-3c from 2 and 1b-1c (Table II, runs 1-2). Similarly to **3a**, **3b** and **3c** were prepared as follows: **3b** (from **1b** (0.17g, 0.6mmol) and **2** (0.25g, 1.2mmol)): ^{1}H-NMR (δ, ppm) 0.49-1.62 (hexyl, 52H), 7.38-8.04 (C_6H_4, 4H), 8.26 (-CH=N-, s, 2H); IR (cell, in $CDCl_3$) 2923, 2857, 1646, 1461, 1255, 1081, 848cm^{-1}. **3c** (from **1c** (0.32g, 0.9mmol) and **2**(0.39g, 1.8mmol)): ^{1}H-NMR (δ, ppm) 7.45-8.09 (aromatic, 8H), 0.43-1.61 (hexyl, 52H); IR (cell, in $CDCl_3$) 2922, 2860, 1776 1458, 1295, 1056, 848cm^{-1}. **3b** was also prepared from **1b** (0.22g, 0.8mmol) and **6** (0.34g, 1.62mmol) in a similar manner (Table III, run 4).

Synthesis of 9a-10a from 1a and 7-8 (Table III, runs 2-3). Similarly to **3a**, **9a** and **10a** were prepared as follows: **9a** (from **1a** (0.21g, 0.76mmol) and **7** (0.16g, 1.6mmol)): ^{1}H-NMR (δ, ppm) 0.88 (ethyl, 20H), 7.83 (C_6H_4,4H), 8.26 (-CH=N-, s, 2H); IR (cell, in $CDCl_3$) 2925, 2862, 1642, 1460, 1376, 1266, 1052, 846 cm^{-1}. **10a** (from **1a** (0.28g,1.0mmol) and **8** (0.46g, 2.2mmol)): ^{1}H-NMR (δ, ppm) 0.75-2.05 (cyclohexyl, 48H), 7.86 (C_6H_4,4H), 8.26 (-CH=N-, s, 2H); IR (cell, in $CDCl_3$) 2921, 2847, 1803, 1643, 1447, 1372, 1255, 1081, 850 cm^{-1}.

Synthesis of 9b-10b from 1b and 7-8 (Table 3, runs 5-6). Similarly to **3a**, **9b** and **10b** were prepared as follows: **9b** (from **1b** (0.22g, 0.8mmol) and **7** (0.16g, 1.6mmol)): ^{1}H-NMR (δ, ppm) 0.86 (ethyl, 20H), 7.50-7.98 (C_6H_4, 4H), 8.28 (-CH=N-, s, 2H); IR (cell, in $CDCl_3$) 2950, 2874, 1647, 1461, 1344, 1254, 1073, 844cm^{-1}. **10b** (from **1b** (0.22g, 0.8mmol) and **8** (0.34g, 1.6mmol)): ^{1}H-NMR (δ, ppm) 0.76-2.03 (cyclohexyl, 48H), 7.32-7.83 (C_6H_4, 4H), 8.26 (-CH=N-, s, 2H); IR (cell, $CDCl_3$) 2919, 2847, 1807, 1644, 1447, 1322, 1256, 1080, 845cm^{-1}.

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Chapter 6

Novel Boron-Containing Polymers and Related Reactions

ABSTRACT

For the further exploration to obtain boron-containing polymers and to extend the methodology developed in the previous chapters in this thesis, haloboration polymerization of diynes, hydroboration reaction of end-double bond polymers, dehydrogenation polymerization of monoalkylborane with diols, and a coupling polymerization of bifunctional organoboron compounds mediated with silver(I) are described.

In 6-1, a polyaddition reaction between boron tribromide and terminal diynes (i.e., "Haloboration Polymerization) is described as a novel methodology for the preparation of organoboron polymers having the unique character as poly(Lewis acid)s. The polyaddition between 1,7-octadiyne and boron tribromide produced a poly(organoboron halide) as a brown solid. This polymer was soluble in common organic solvents such as chloroform and dichloromethane. The molecular weight of the obtained polymer was measured by GPC, from which M_n and M_w were found to be 5,200 and 15,500, respectively. The structure of the polymer was supported by its ^{1}H-, ^{11}B-NMR, IR and UV spectra. The present haloboration polymerization was proved to proceed by *cis*-addition of B-Br to C≡C. During the precipitation of the polymer into ethanol, the B-Br moieties in the polymer were completely replaced by B-OEt moieties. Similarly, the reaction of the polymer with diol or with H_2O caused a gelation. The B-Br bond in the polymer was subjected to the further haloboration reaction with phenylacetylene. The characteristic property of the polymer as a poly(Lewis acid) was also demonstrated by the reaction with THF to produce 4-bromo-1-butanol after hydrolysis.

6-2 describes the hydroboration reaction of the terminal double bond of polystyrene with thexylborane to produce polymers bearing one organoboron unit at the center of the polymer. The molecular weight of the resulting polymer was duplicated as a result of hydroboration in comparison with the starting polymer. The obtained polymer was subjected to a novel polymer reaction with α,α-dichloromethyl methyl ether (DCME) followed by the oxidative treatment. A polymer having one tertiary alcohol unit at

the center of the polymer chain was produced without obvious decrease of the molecular weight.

For the preparation of novel boron-containing polymers, dehydrogenation reaction between bifunctional hydroborane compounds, i.e., thexylborane and diols to produce novel boronate oligomers is described in 6-3. When the reaction of thexylborane with an equimolar amount of 1,6-hexanediol was carried out at room temperature for 1 day, a colorless wax was obtained after removing the solvent. The cryoscopic measurement of the molecular weight of the obtained wax indicated the formation of oligomeric species. This oligomer was purified by coagulation with *n*-pentane, and characterized by spectroscopic analyses. The thermal stability of the resulting boronate oligomer is also described.

6-4 describes a novel polymerization by means of radical coupling reaction of telechelic organoboron compounds using silver(I) salt. Telechelic organoboron compounds were prepared by hydroboration of dienes and reacted with silver(I) nitrate under alkaline conditions. Organoboron compounds prepared from terminal dienes such as 1,7-octadiene or *p*-divinylbenzene gave only low molecular weight oligomeric coupling products due to the disproportionation of alkyl silvers or alkyl radicals. On the other hand, when dienes were designed as to favor the formation of benzylic boranes at the hydroboration stage, the molecular weights of the corresponding polymers after coupling reactions were extremely higher in comparison with those of the polymers from terminal dienes. For instance, M_n and M_w of the polymer prepared from *β,β,β',β'*-tetramethyl-*p*-divinylbenzene were 42,200 and 116,500, respectively.

Chapter 17

Haloboration Polymerization. Novel Organoboron Polymers by Polyaddition between Boron Tribromide and Terminal Diyne.

Introduction

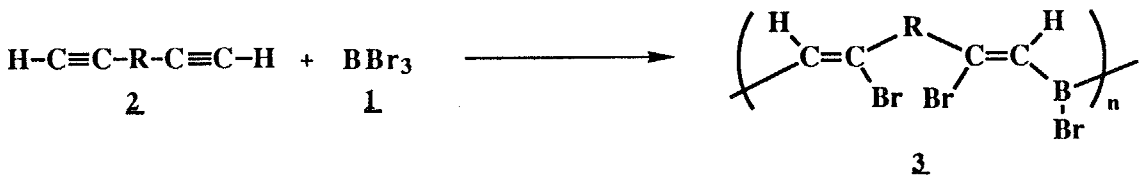
Substituted boron halides are useful reagents for ether cleavage1), and selective haloboration reactions2) under mild conditions. Polymeric homologues of these materials, therefore, may have a potential to show unique characteristic properties as novel reactive polymers. However, such polymers have scarcely ever been investigated.

In Chapter 2, the author has described hydroboration polymerization, in which novel organoboron polymers were prepared by polyaddition between monoalkylborane and diene compounds. The resulting organoboron polymers were demonstrated as reactive polymers by the several kinds of migration reactions to produce poly(alcohol), poly(ketone), and so on, as described in Chapter 3.

Haloboration reaction is coming to be known to provide key intermediates for the synthesis of substituted olefins3). This reaction proceeds chemoselectively and stereoselectively under the appropriate conditions4). The reactivity of a boron-halide moiety towards haloboration is known to be decreased with the decrease of its Lewis acidity as in the following general order; $BX_3 > RBX_2 > R_2BX$. Especially, dialkenylboron bromide, which may be produced at first by the haloboration between BBr_3 and diyne, has low Lewis acidity due to two alkenyl groups on the boron atom. Accordingly, a large different reactivity between BBr_3 and dialkenylboron bromide may make it possible to form a linear polymer without gelation by supplying two B-Br bonds from boron tribromide.

First of all, as a typical and preliminary example, haloboration polymerization between boron tribromide (**1**) and terminal diynes (**2a**-**2e**) (i.e., "Haloboration Polymerization") has been examined (Scheme I). The resulting polymer still has boron-bromide moiety in its structure. This means that the organoboron polymers prepared by haloboration polymerization can be regarded not only as poly(Lewis acid)s, but also as a novel type of reactive polymer.

Scheme I



Results and Discussion

Polymerization was carried out by adding an equimolar amount of 1,7-octadiyne (**2a**) to a 1.0M dichloromethane solution of **1** with vigorous stirring at -78°C under nitrogen. The reaction mixture was warmed gradually to room temperature. From the result of GC analysis, conversion of **2a** was quantitative. After coagulation with dry *n*-pentane under nitrogen, the polymer (**3a**) was isolated as a brown solid in 90% yield.

The structure of the obtained polymer (**3a**) was supported by spectroscopic analyses. Figure 1 represents the ^{1}H-NMR of **3a**, in which vinyl protons, methylene protons adjacent to vinyl group, and inner methylene protons were observed. Integral ratios of these peaks were in good agreement with the calculated values for the expected structure.

Referred to the previous report of Blackborow4), the chemical shift of the vinyl protons (δ=6.69ppm) indicates *Z* structure of **3a** (*vide infra*). In its IR spectrum, the strong peak at 1580cm^{-1} assignable to the stretching of the electron deficient C=C was observed, while no peaks due to the terminal acetylene were detected. The molecular weight of **3a** was measured by GPC ($CHCl_3$ as an eluent) using polystyrene calibration curves, from which M_n and M_w were found to be 5,200 and 17,000, respectively. After the measurement of GPC, however, the structure of the polymer was proved to be changed into **4a** from its ^{1}H-NMR analysis. That is, B-Br moiety was replaced by B-OEt3,5,6). This result may be explained by the reaction of **3a** with a small amount of ethanol, which usually contaminates $CHCl_3$ as a stabilizer. This was also observed when **3a** was precipitated into ethanol (*vide infra*).

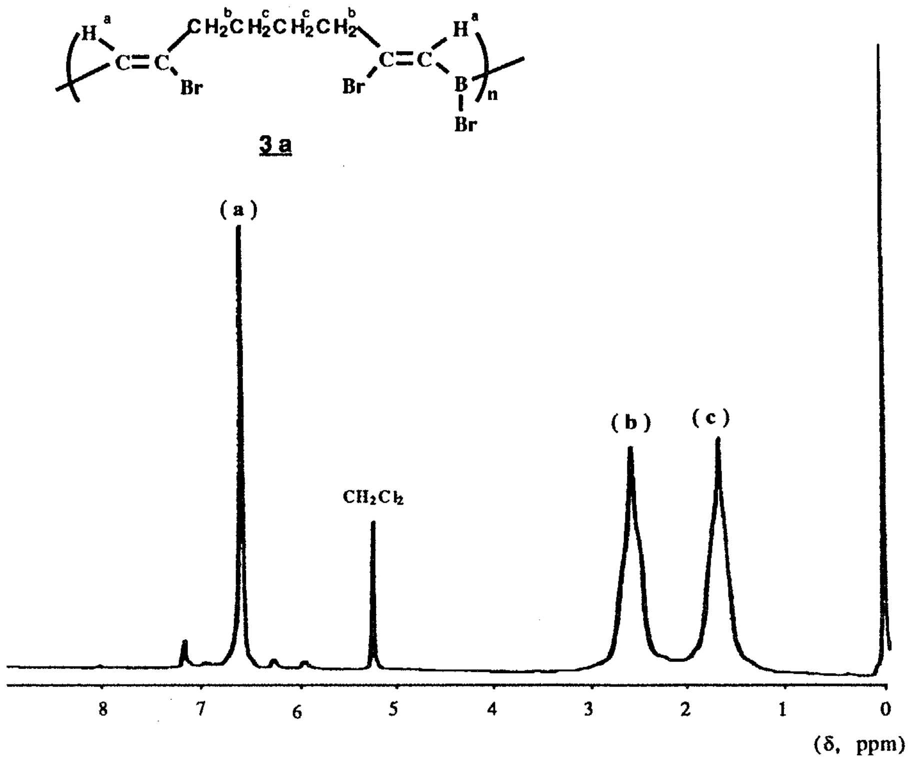


Figure 1 ^{1}H-NMR spectrum of 3a.

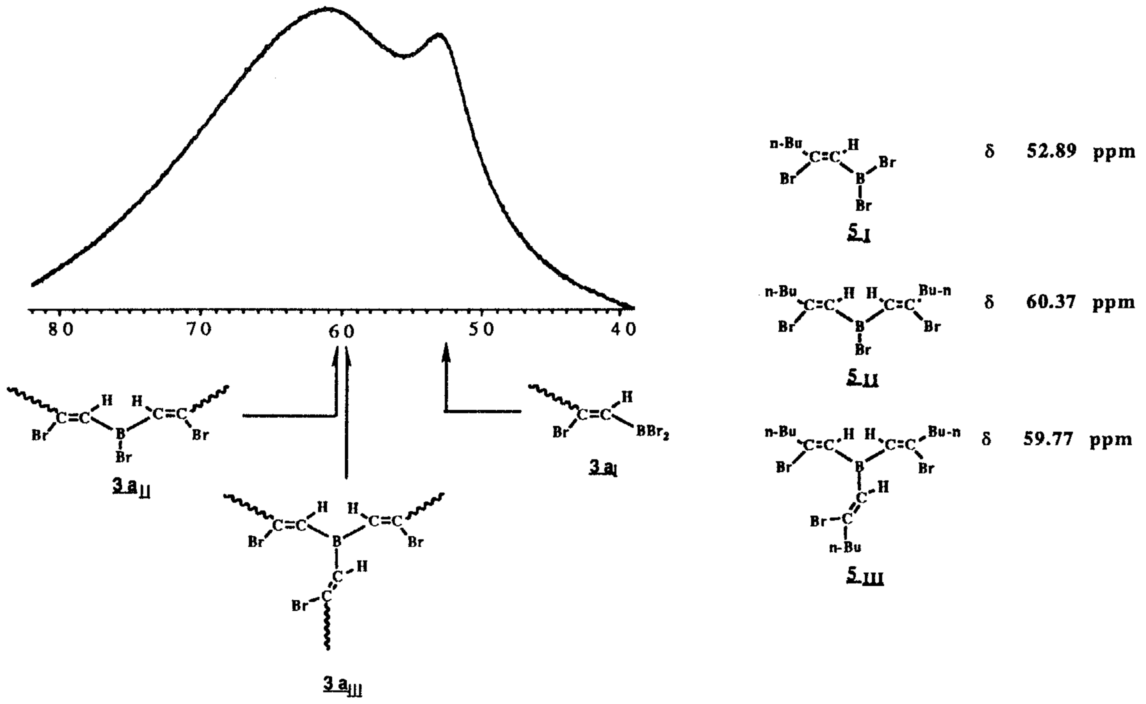
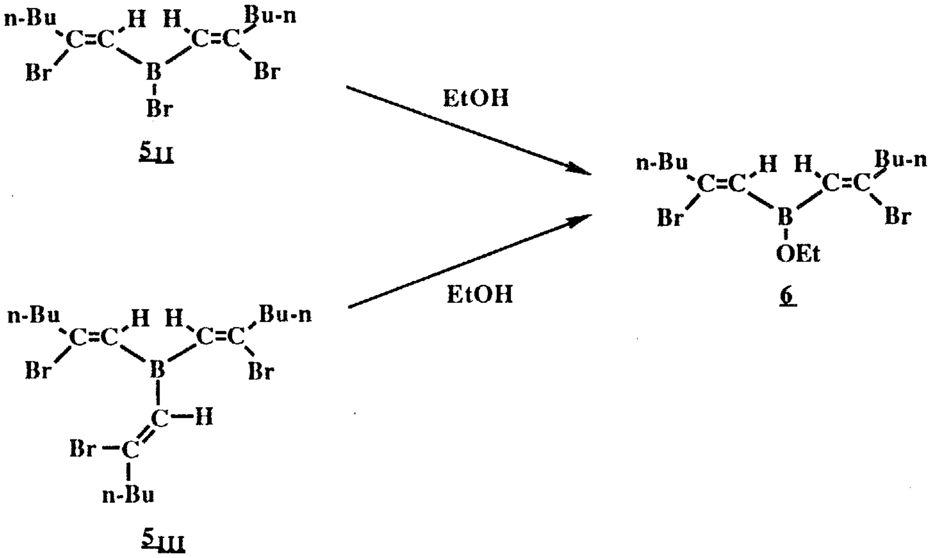


Figure 2 ^{11}B-NMR spectrum of 3a.

^{11}B-NMR and UV spectra provided significant information regarding the contribution of branched structure in the main chain of the polymer. For this purpose, three compounds (**5**$_{I}$-**5**$_{III}$)$^{4)}$ were prepared as models for the corresponding polymer structures (**3a**$_{I}$-**3a**$_{III}$), respectively. As illustrated in Figure 2, **5**$_{I}$ (polymer end model), **5**$_{II}$ (main chain model), and **5**$_{III}$ (branched structure model) showed resonances at 52.9, 60.4, and 59.8ppm, respectively. On the other hand, the polymer (**3a**) showed a resonance at 60.8ppm accompanying a shoulder peak at 52.9ppm. Thus, the former (main) peak of **3a** can be assigned to the boron atom in the main chain (linear or branched), and the latter (shoulder) to that of the chain end. From the ratio of intensities of these two peaks by assuming that the polymer has only two end groups, i.e., a linear structure, the molecular weight of **3a** was calculated to be of the same order as the value estimated by GPC. This result shows a very small contribution of the branched structure (**3a**$_{III}$) in the polymer. It should also be noted that no gelation was observed during haloboration polymerization.

Scheme II

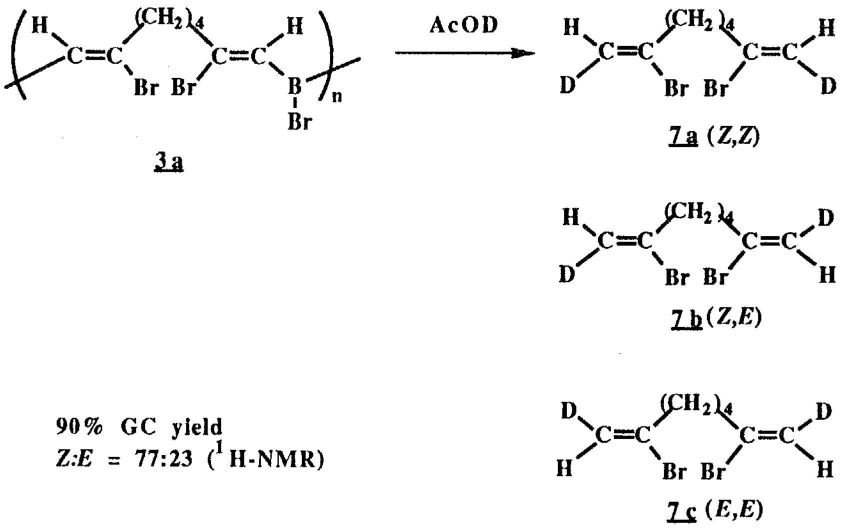


From either **5**$_{II}$ or **5**$_{III}$, the same product (**6**) was afforded by the reaction with ethanol (Scheme II). This result indicates that one B-C bond in trialkenylborane (**5**$_{III}$) is reactive to ethanol to form B-OEt similarly to B-Br in **5**$_{II}$. Accordingly, if the polymer (**3a**) has a branched structure of trialkenylborane moiety (**3a**$_{III}$) even in a small amount as mentioned above, a scission of B-C bonds should take place at this point under the conditions of GPC measurement. It may be possible that the molecular weight of the generated polymer before GPC measurement was higher in comparison with that estimated by GPC.

The structure of **3a** was further confirmed by UV measurement. The polymer (**3a**) and its model compound ($\mathbf{5}_{\mathrm{II}}$) showed the same absorption maxima at 255nm, which is assignable to the C=C-B-C=C moiety. By using a molar absorptivity for $\mathbf{5}_{\mathrm{II}}$, this structure was proved to exist almost quantitatively in **3a**.

To elucidate the stereochemistry of haloboration polymerization, acid hydrolysis of **3a** with deuterated acetic acid was examined. 2,7-Dibromo-1,8-dideuterio-1,7-octadiene (**7**) was obtained in 90% yield (GC). From the results of ^{1}H-NMR analysis, as shown in Scheme III, more than 77% of **7** was proved to contain the *Z*-isomer. This result is taken to mean that the present haloboration polymerization proceeds mainly in the *cis*-addition of boron-bromide to terminal acetylene.

Sheme III



3a

7a (*Z*,*Z*)

7b (*Z*,*E*)

90% GC yield
Z:*E* = 77:23 (^{1}H-NMR)

7c (*E*,*E*)

The results of haloboration polymerization between **1** and **2a** by changing the feed ratio of **2a** to **1** are summarized in Table I. The molecular weight of the obtained polymer was increased when the feed ratio approached or slightly exceeded unity. As expected, a gelation was observed when excess **2** was used for this polymerization (Run 6). The obtained gel in this experiment became soluble after the treatment with ethanol. The soluble product showed lower molecular weight (GPC, M_n=4,100, M_w=12,100) than that of the polymer prepared by 1:1 feeding. This finding supports the assumption that one boron-carbon bond of the trialkenylborane moiety in the gel was cleaved by ethanol as described before.

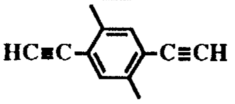
Table I Dependence of Molecular Weight on the Feed Ratio of 2a/ 1.[a)]

Run	1 g (mmol)	2a g (mmol)	2a/1	M.W.[b)]
1	0.320 (1.28)	0.102 (0.96)	0.75	830
2	0.278 (1.11)	0.100 (0.94)	0.85	3,320
3	0.423 (1.69)	0.169 (1.59)	0.94	6,420
4	0.526 (2.10)	0.225 (2.11)	1.00	15,500
5	0.403 (1.61)	0.178 (1.67)	1.04	28,000
6	0.489 (1.95)	0.228 (2.15)	1.10	-[c)]

a) Reactions were carried out in CH_2Cl_2 at -78°C, and then warmed up to r.t.
b) GPC ($CHCl_3$, Polystyrene standard), peak top molecular weight.
c) Gelation was observed, when the system was warmed up to 0°C.

Haloboration Polymerization between 1 and Various Terminal Diynes. Aliphatic terminal diynes such as 1,8-nonadiyne (**2b**), 1,9-decadiyne (**2c**) were also subjected to haloboration polymerization. From both **2b** and **2c**, soluble poly(organoboron halide)s were obtained. On the other hand, when 1,4-diethynylbenzene (**2d**) or 2,5-dimethyl-1,4-diethynylbenzene (**2e**), in which C≡C was conjugated to aromatic rings, was used as a monomer, the deposition of the polymer during polymerization was observed. The obtained polymers were insoluble in chloroform or dichloromethane. After treatment with ethanol, however, these polymers became soluble in chloroform. The results of haloboration polymerization using various diynes followed by the treatment with ethanol are summarized in Table II.

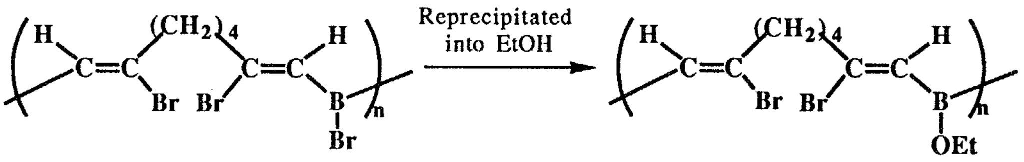
Table II Haloboration Polymerization between BBr_3 and Various Diynes.

Run	Diyne (2)		[2]/[1]	Yield[a)] (%)	$\overline{M}_n$[b)]	$\overline{M}_w$[b)]
1	$HC\equiv C(CH_2)_5C\equiv CH$	(b)	1.01	86	6,740	32,400
2	$HC\equiv C(CH_2)_6C\equiv CH$	(c)	1.01	91	7,230	26,600
3		(d)	1.00	92	990	1,660
4		(e)	1.00	69	700	1,370

a) Isolated yields after reprecipitation into EtOH.
b) GPC ($CHCl_3$), polystyrene standard.

Reactions of Poly(organoboron halide)s. The reactivity of B-Br in **3a** was demonstrated as follows. When the polymer (**3a**) was precipitated into ethanol, a polymer with the structure of **4a** was obtained in 93% yield (Scheme IV).

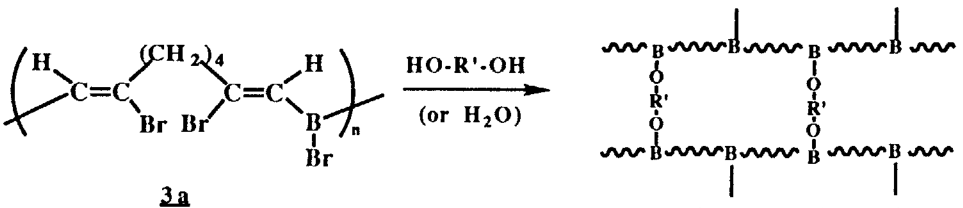
Scheme IV



3a 4a

In a manner similar to this, **3a** was reacted with water or diol compounds such as ethylene glycol to produce the corresponding gel by the intermolecular substitution reaction as illustrated in Scheme V.

Scheme V

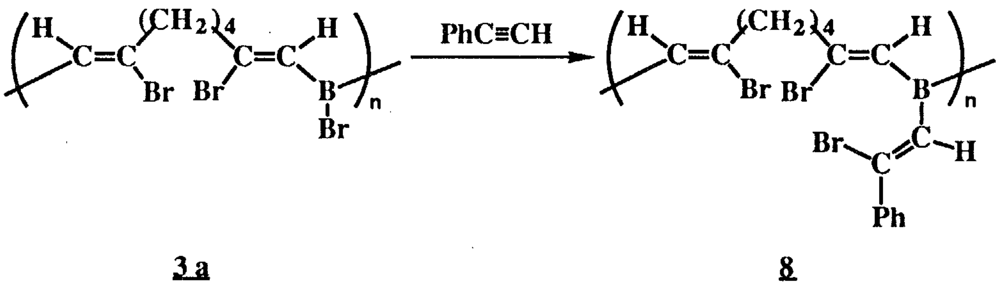


3a

Polymeric Network

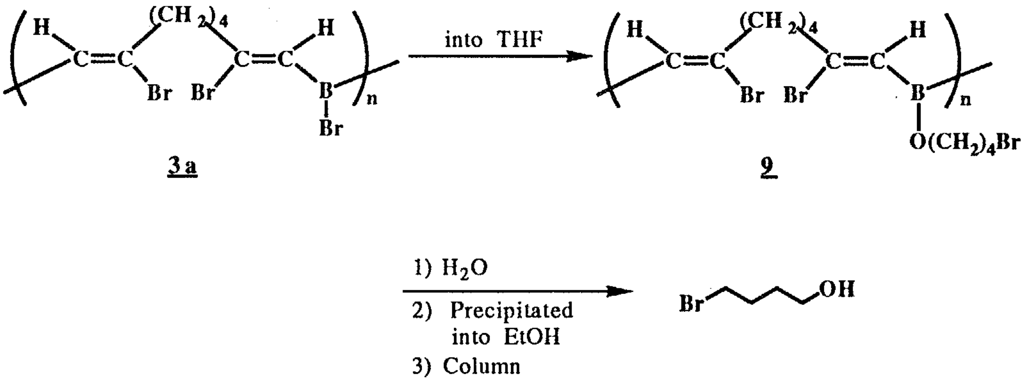
Terminal monoyne compounds such as phenylacetylene were added to a dichloromethane solution of **3a**. In this reaction, a further haloboration occurred to produce **8** as shown in Scheme VI. The formation of **8** was supported by its ^{1}H-NMR spectrum, although **8** was decomposed during GPC measurement.

Scheme VI



3a was also subjected to the ether cleavage reaction. For example, when excess THF was introduced into a dichloromethane solution of **3a** at 0°C, the polymer structure was found to be changed into **9** (Scheme VII) by its ^{1}H-NMR. After hydrolysis of **9**, followed by purification with SiO_2 column chromatography, 4-bromo-1-butanol was isolated in 90% yield. This reaction also demonstrates the characteristic property of **3a** as a poly(Lewis acid).

Scheme VII



Experimental Section

Materials and Instruments. Boron tribromide (**1**) was purified by distillation. Dichloromethane and chloroform were dried over P_2O_5 and distilled before use. **2a**-**2c** were purified by distillation. **2d** and **2e** were prepared as previously described[8].

^{1}H-NMR and ^{11}B-NMR spectra were recorded in $CDCl_3$ on a Hitachi R-600 (60MHz) instrument and JEOL JNM-JX-400 instrument, respectively. IR spectra were obtained on a Perkin Elmer 1600 spectrometer. UV spectra were measured on a Hitachi 200 UV-VIS spectrophotometer. Gas chromatographic analysis was made on a Simadzu GC-6A instrument. Gel permeation chromatographic analyses were carried out on a Jasco Triroter (Shodex AC803, $CHCl_3$) by using chloroform as an eluent after calibration with standard polystyrene samples.

Haloboration Polymerization between 1,7-Octadiyne (2a) and BBr_3 (1). To a 1.0M dichloromethane solution of **1** (0.526g, 2.10mmol), **2a** (0.225g, 2.11mmol) was added with vigorous stirring at -78°C under nitrogen. The reaction mixture was then warmed gradually to room temperature. After reprecipitation into 40ml of dry *n*-pentane under nitrogen, 0.670g of the polymer (**3a**) was isolated as a brown solid in 90% yield. IR; 2940, 1580cm^{-1}. All the other spectroscopic data are shown in Results and Discussion.

After the polymer (**3a**) prepared from 0.517g (2.06mmol) of **1** and 0.218g (2.05mmol) of **2a** was precipitated into ethanol under nitrogen, **4a** (0.611g) was obtained as a greenish white gum in 93% yield. ^{1}H-NMR (δ, ppm) 1.27 (CH_3-C-O-, t, 3H), 1.62 (-CH_2-C-C=C, m, 4H), 2.54 (-CH_2-C=C, m, 4H), 4.09 (-O-CH_2-, q, 2H), 6.24 (C=CH-B, 2H). IR (cell, $CHCl_3$) 2950, 1640cm^{-1}.

Acid Hydrolysis of 3a. To a dichloromethane solution of **3a** prepared from 0.344g (1.37mmol) of **1** and 0.147g (1.38mmol) of **2a**, dodecane (0.099g, 0.58mmol) was added as an internal standard. At 0°C, 1ml of deuterated acetic acid was added. After standing for 2 days at room temperature, **7** was detected in 90% yield (GC). After purification with SiO_2 column, stereochemistry of **7** was examined by ^{1}H-NMR analysis. ^{1}H-NMR (δ, ppm) 1.56 (-CH_2-C-C=C, m, 4H), 2.45 (-CH_2-C=C, m, 4H), 5.40 (*E* CH=C-) 5.57 (*Z* CH=C-) (total 2H, *Z*>77%); IR (cell, $CHCl_3$) 2940, 1604cm^{-1}.

Haloboration Polymerization using Various Terminal Diynes. Various poly(organoboron halide)s were obtained in a similar manner to that from 1,7-octadiyne, and were subjected to the reaction with ethanol. **4b** (from 0.451g, 1.80mmol of **1** and

0.218g, 1.81mmol of **2b**): Yield 0.520g (86%); ^{1}H-NMR (δ, ppm) 1.27 (CH_3-C-O-, t, 3H), 1.47 (-CH_2-C-C=C, m, 6H), 2.52 (-CH_2-C=C, m, 4H), 4.07 (-O-CH_2-, q, 2H), 6.22 (C=CH-B, 2H); IR (cell, $CHCl_3$) 3015, 2977, 2940, 1620, 1335, 1046cm^{-1}. **4c** (from 0.505g, 2.02mmol of **1** and 0.274g, 2.04mmol of **2c**): Yield 0.643g (91%); ^{1}H-NMR (δ, ppm) 0.92-1.94 (CH_3-C-O-, -CH_2-C-C=C, total 11H), 2.52 (-CH_2-C=C, m, 4H), 4.03 (-O-CH_2-, q, 2H), 6.22 (C=CH-B, 2H); IR (cell, $CHCl_3$) 2980, 2940, 1620, 1335, 1045cm^{-1}. **4d** (from 0.522g, 2.08mmol of **1** and 0.263g, 2.09mmol of **2d**): Yield 0.657g (92%); ^{1}H-NMR (δ, ppm) 1.35 (CH_3-C-O-, t, 3H), 4.17 (-O-CH_2-, m, 2H), 6.99 (C=CH-B, 2H), 7.67 (C_6H_4, s, 4H); IR (cell, $CHCl_3$) 3011, 2980, 1597, 1335, 1127cm^{-1}. **4e** (from 0.473g, 1.89mmol of **1** and 0.291g, 1.89mmol of **2e**): Yield 0.657g (92%); ^{1}H-NMR (δ, ppm) 1.39 (CH_3-C-O-, t, 3H), 2.42 (CH_3-Ph, br s, 6H), 4.21 (-O-CH_2-, m, 2H), 6.55 (C=CH-B, 2H), 7.18 (C_6H_2, s, 4H); IR (cell, $CHCl_3$) 3010, 2979, 1623, 1333, 1032cm^{-1}.

Reaction of 3a with Ethylene Glycol. To a brown dichloromethane solution of **3a**, a dichloromethane solution of ethylene glycol was added. A purple gel was obtained within a few seconds.

Reaction of 3a with Phenylacetylene. To a dichloromethane solution of **3a** prepared from 0.259g (1.03mmol) of **1** and 0.107g (1.01mmol) of **2a**, phenylacetylene (0.147g, 0.144mmol) was added at -78°C, and the reaction mixture was allowed to be warmed to room temperature. After evaporating the solvent, **8** was obtained in a quantitative yield. ^{1}H-NMR (δ, ppm) 1.68 (-CH_2-C-C=C, m, 4H), 2.60 (-CH_2-C=C, m, 4H), 6.59-7.05 (-C-CBr=CH-, 2H), 7.10-7.92 (C_6H_5-CBr=CH-, m, 6H). IR (cell, $CHCl_3$) 2940, 1580cm^{-1}.

Reaction of 3a with Tetrahydrofuran. To a dichloromethane solution of **3a** prepared from 0.553g (2.21mmol) of **1** and 0.236g (2.22mmol) of **2a**, tetrahydrofuran (2ml) was added at -78°C, and the reaction mixture was allowed to be warmed to room temperature. After evaporating the solvent, **9** was obtained in a quantitative yield. **9**: ^{1}H-NMR (δ, ppm) 1.62 (-CH_2-C-C=C, m, 4H) 1.84 (-O-C-CH_2CH_2-C-Br, m, 4H), 2.54 (-CH_2-C=C, m, 4H), 3.47 (-CH_2Br, t, 2H), 4.07 (-CH_2-O-B, t, 2H), 6.24 (-C-CBr=CH-, 2H); IR (cell, $CHCl_3$) 2940, 1610, 1340cm^{-1}. After adding 5ml of water, the product was extracted with three 10ml portions of diethyl ether. The organic layer was concentrated, and then precipitated into ethanol (20ml). The ethanol suspension was passed through a silica gel column to isolate the product. 4-Bromo-1-butanol (**9**) was obtained as a colorless oil7) (yield: 90%).

References and Notes

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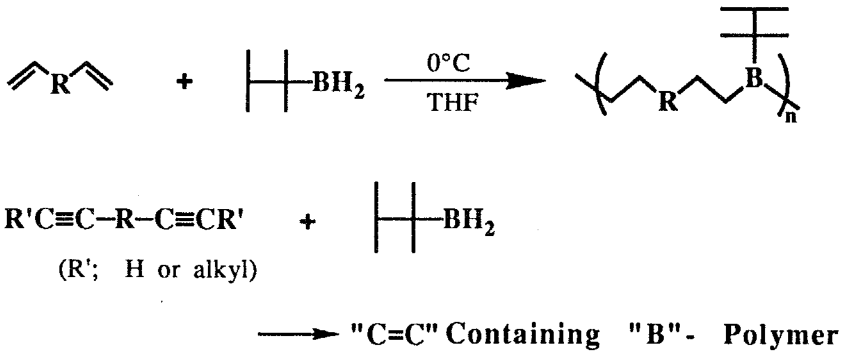
6 - 2

Hydroboration of Styryl-Terminated Polystyrene.

Introduction

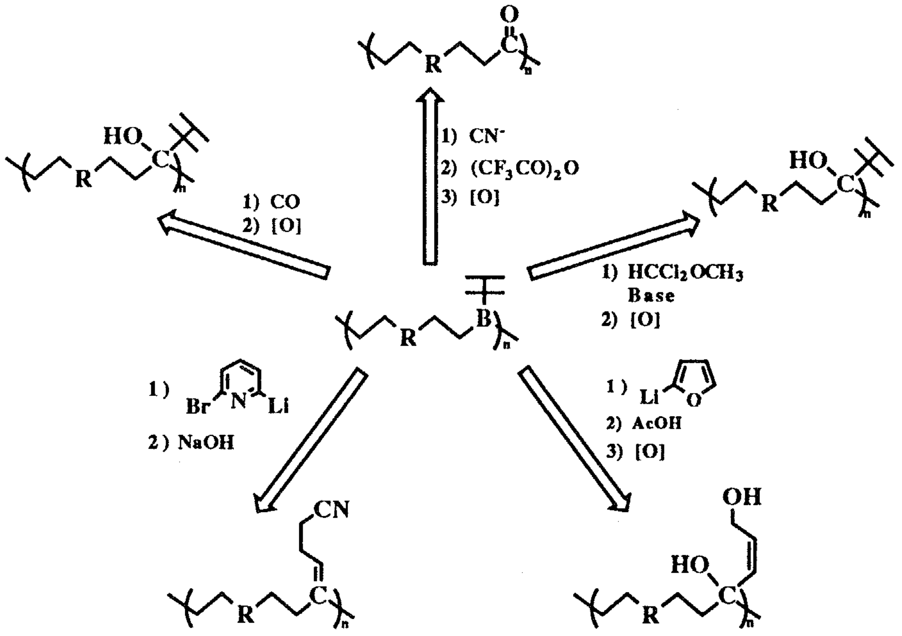
As described in Chapter 2, organoboron polymers in which trialkylborane units were linked in the main chain of the polymer were produced by the hydroboration polymerization between thexylborane and bifunctional unsaturated compounds such as dienes and diynes (Scheme I). The organoboron polymers thus obtained were examined to be converted to various kinds of functional polymers by the novel polymer reactions which have been described in Chapter 3 (Scheme II). These novel polymer reactions show the new synthetic methodology to obtain various functional polymers whose structures are difficult to build up by the conventional polymer synthetic methods.

Scheme I

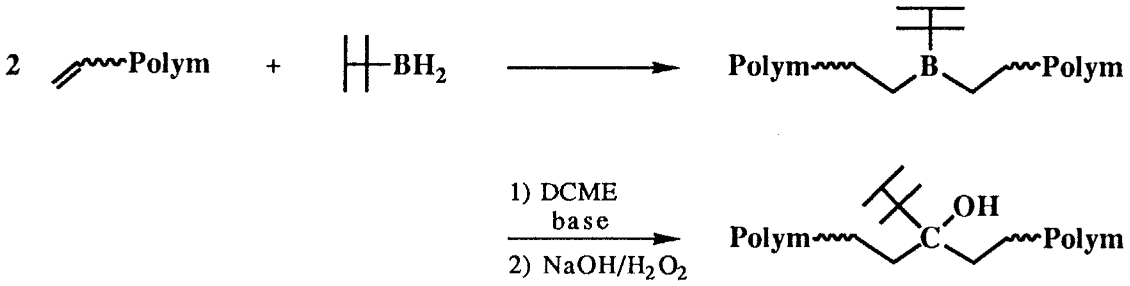


Thexylborane has two B-H bonds and generally acts as a bifunctional hydroborane. If hydroboration reaction with this thexylborane is subjected to the terminal double bonds of polymers, polymeric organoboron species in which only one organoboron unit is located at the center of the main chain can be produced. In the case of anionic living polymerization of styrene, end-capping reactions with halosilanes were examined to produce molecular-designed polystyrenes in which the number of the polystyrene arms was successfully controlled$^{1)}$. However, the resulting polymers were not examined to be converted to the functional polymers because of the low reactivity of the silicon-carbon bond. The polymers bearing organoboron unit in the main chain of the polymer produced by the present method may have such a potential, since they can be regarded as an organoboron compound having long arms. Thus, the hydroboration reaction of the terminal double bond of polystyrene and the reaction of the resulting polymer with DCME are described here (Scheme III).

Scheme II



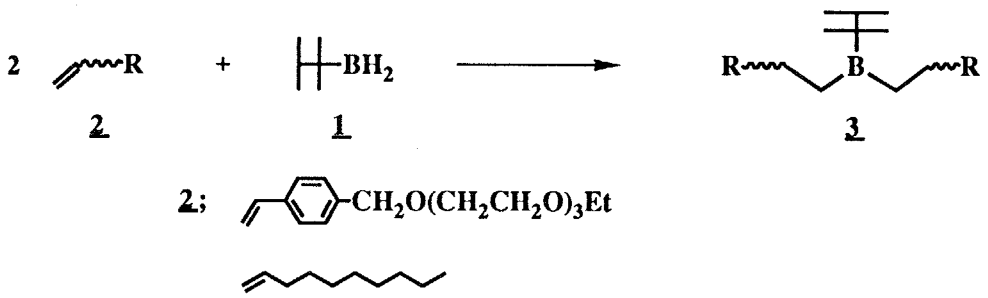
Scheme III



Results and Discussion

As a model reaction for the present study, hydroboration reactions of thexylborane (1) with mono-olefins having relatively longer alkyl chains were first examined. When **1** was reacted with 2 molar equivalents of styryl ether (**2**), the resulting organoboron compound (**3**) showed unimodal peak in GPC using dried THF as an eluent (Scheme IV, Figure 1). No peak was detected around that for the starting olefin (**2**). The same result was also obtained from the reaction of 1-decene with **1**. These results show the possibility to obtain the two-armed polymer from **1** and the double bond-terminated polymer.

Scheme IV



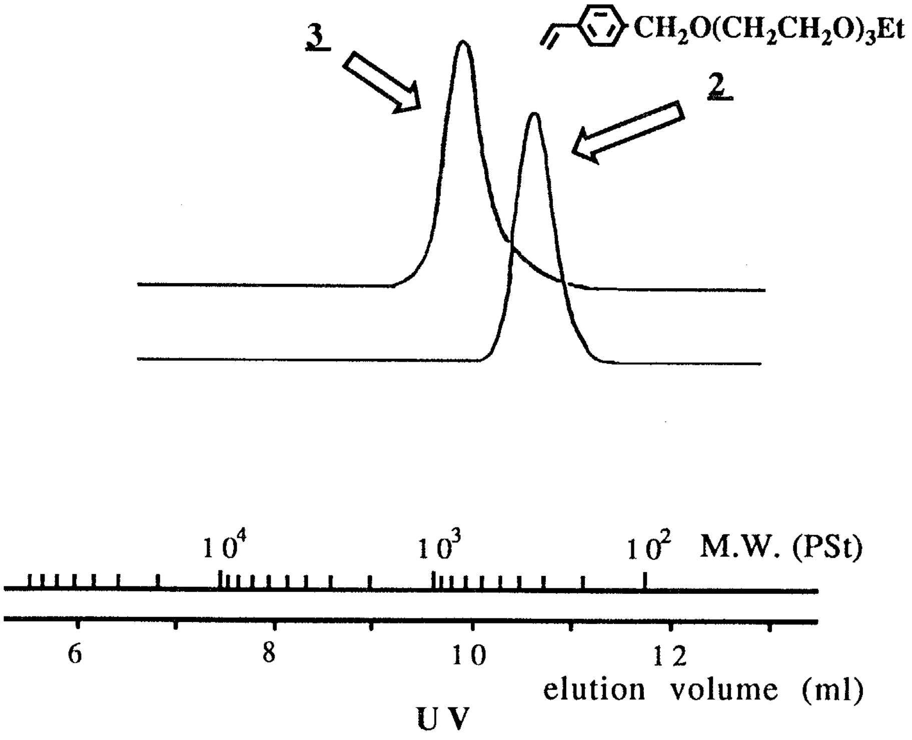
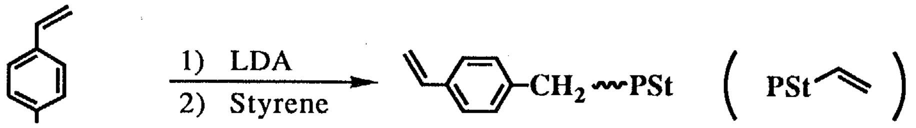


Figure 1 GPC traces of **2** and **3**.

Due to the synthetic facility and the high enough functionality, the styryl-terminated polystyrene (**4**) obtained by the anionic equilibrium polymerization reported by Nagasaki *et al.* [2]) was used for the present study (Scheme V). The obtained **4** was fractionated by the precipitation with methanol/THF system.

Scheme V



4

When the fractionated **4** was reacted with **1**, the molecular weight of the resulting polymer (**5**) in GPC was found to be shifted to higher molecular weight region. For instance, when **4** (M_n=1,130, M_w=2,040) was reacted with **1**, M_n and M_w of the resulting **5** were 2,030 and 3,360, respectively (Figure 2). Although it is difficult to mention that the efficiency of hydroboration reaction was perfect, it is clear that most of the starting polymer was found to be jointed effectively by the thexylborane moiety.

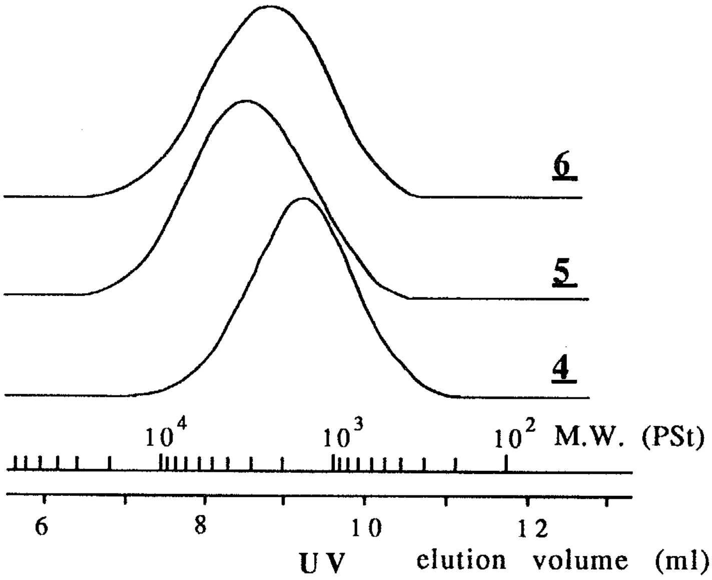
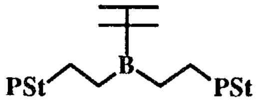
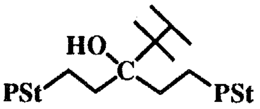


Figure 2 GPC traces of 4, 5, and 6.

The obtained polymer having organoboron unit (**5**) was reacted with DCME followed by the oxidation. Without any purification such as reprecipitation, the peak of the resulting polymer (**6**) in GPC appeared to be a unimodal one, and M_n and M_w of **6** were 1,720 and 2,750, respectively. Though these values are a little bit smaller than those of **5**, it should be noted that most part of polymer having organoboron unit was successfully converted to the polymer having alcohol moiety. Without the migration reaction with DCME, organoboron moiety remained in the polymer chain should be cleaved by the oxidative treatment[3], which should result in the formation of the end-alcohol polymer having the molecular weight similar to **4**. Accordingly, small decrease of molecular weight after the reaction might indicate that the small part of **5** was not incorporated to the migration reaction. The results of hydroboration reaction and of the reaction with DCME are summarized in Table I. IR spectrum of **6** indicated the existence of alcohol moiety in the main chain. In the ^{1}H-NMR spectrum of **6**, small peaks attributable to the thexyl groups were observed. The disappearance of the end-styryl groups in **4** also supports the structure of **6** (Figure 3).

Table I **Hydroboration Reactions of Styryl-Terminated Polystyrene with Thexylborane followed by the Reaction with DCME[a].**

 4		 5		 6	
$M_n^{b)}$	$M_w^{b)}$	$M_n^{c)}$	$M_w^{c)}$	$M_n^{b)}$	$M_w^{b)}$
520	680	930	1,200	900	1,160
1,130	2,040	2,030	3,360	1,720	2,750

a) Hydroboration reaction was carried out at room temperature by the addition of 1 to the THF solution of 4 by using a microfeeder.
b) GPC (THF), polystyrene standard.
c) GPC (dry THF), polystyrene standard.

Though this section deals only the synthesis and one example of the conversion reaction of polymer having one organoboron moiety in its main chain, there are numerous possibilities to convert to the polymers bearing various kinds of functional groups on the basis of organoboron chemistry. In other word, the present polymer reaction may offer a useful synthetic method for the macromolecular design and synthesis.

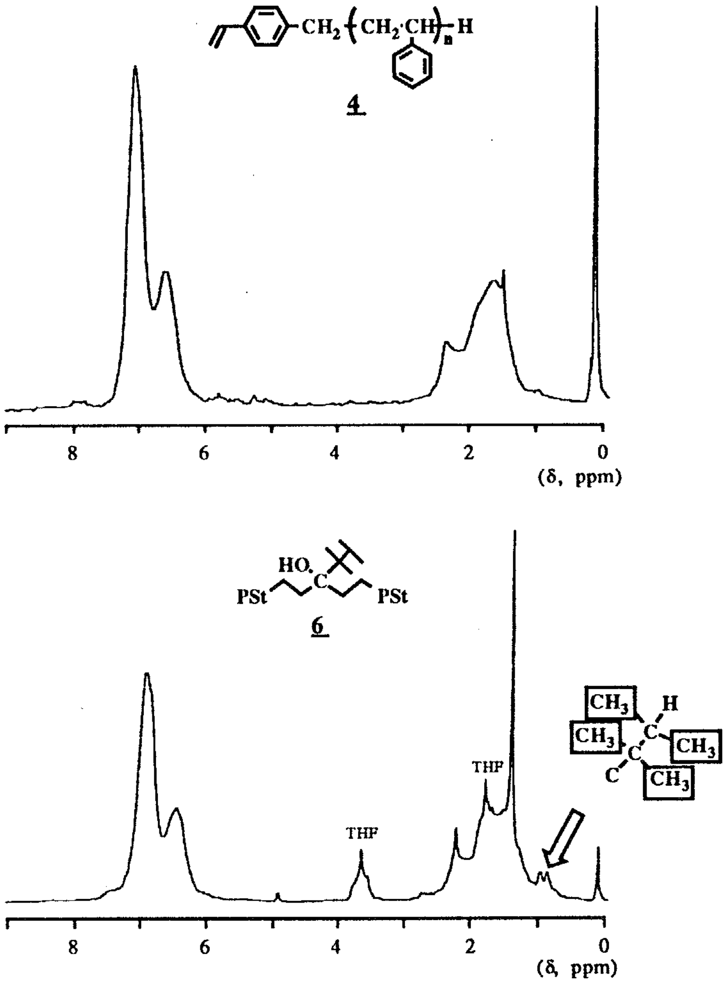


Figure 3 ^{1}H-NMR spectra of 4 and 6.

Experimental Section

Materials and Instruments. Tetrahydrofuran was dried over lithium aluminum hydride and was distilled before use. Thexylborane was prepared from 2,3-dimethyl-2-butene and $Me_2S \cdot BH_3$ as reported earlier$^{4)}$ and was purified by distillation$^{5)}$. Styryl ether (2) was prepared from *p*-chloromethylstyrene, triethylene glycol monoethyl ether, and sodium hydride, and was purified by distillation. 1-Decene was purified by distillation. Styryl-terminated polystyrene was prepared by the reported procedure,[2] and was fractionated by the precipitation with methanol/THF followed by the freeze-drying with benzene.

^{1}H-NMR spectra were recorded in $CDCl_3$ on a Hitachi R-600 instrument. IR spectra were obtained on a Perkin Elmer 1600 spectrometer. Gel permeation chromatographic analyses were carried out on a Tosoh HLC-8020 (TSK gel G3000, THF as an eluent) after calibration with standard polystyrene samples. For the GPC measurements of **3** and **5**, dried THF was used as an eluent with constant nitrogen bubbling.

Synthesis of 3. To a 0.5ml THF solution of styryl ether (**2**, 0.145g, 0.49mmol), **1** (0.026g, 0.26mmol) was added by using a microfeeder (15μmol/min.) at ambient temperature under nitrogen. After the complete addition of **1**, the reaction mixture (**3**) was stirred for 1h and was subjected to the GPC measurement.

Hydroboration of Styryl-Terminated Polystyrene (4). To a 1ml THF solution of **4** (0.203g, M_n=1,130, 0.18mmol), **1** (0.012g, 0.12mmol) was added by using a microfeeder (15μmol/min.) at ambient temperature under nitrogen. After the addition of **1** was over, the reaction mixture (**5**) was stirred for 1h and was subjected to the GPC measurement.

Reaction of 5 with DCME. To the THF solution of **5** prepared by the procedure described above, DCME (0.045g, 0.39mmol) and Et_3COLi in *n*-hexane (1.36N, 0.4ml, 0.54mmol) was added at 0°C, and the reaction mixture was kept stirring overnight. After the oxidative treatment with $NaOH/H_2O_2$ at 50°C for 3h, the obtained reaction mixture was extracted with three 20ml portions of THF. When the obtained polymer was precipitated with methanol, 0.192g of **6** was isolated as a white solid.

References

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5) See 2-1.

6 - 3

Boronate Oligomers *via* Dehydrogenation of Diols with Thexylborane.

Introduction

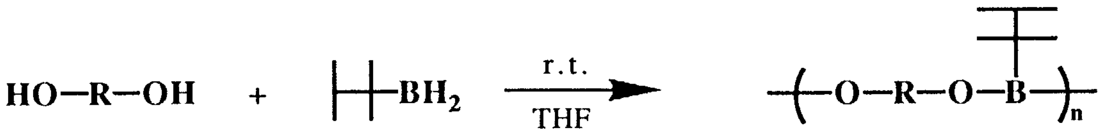
Boron compounds are widely used as a catalyst of polymerization, and as a cross-linking agent of phenolic compounds, poly(vinyl alcohol), and epoxy resin systems1). However, there are few polymers consisting of boron atoms in the main chain, except for borazine, phosphinoborane, and decarborane polymers2). Previously, the borate polymer was produced by the dehydration reaction of tetrahydroxydiphenyl with boric acid2). In this system, the number of functionality of monomers was three or four. The obtained polymer was reported to be partly soluble in *N,N*-dimethylacetamide and showed heat-resistant property.

In this section, new synthetic method to obtain soluble boronate oligomers by the dehydrogenation reaction of diols with thexylborane is described.

Results and Discussion

It is known that boron-hydride is readily substituted by the treatment with alcohols or phenols to produce the corresponding esters of boronic acid3). This reaction can be used for the analysis of B-H species, due to its quantitative conversion3b). Thus, bifunctional thexylborane (**1**) was employed as a monomer, and dehydrogenation between diols and **1** to produce a poly(boronic ester) was examined (Scheme I).

Scheme I



Polymerization condition was examined by using **1** and 1,6-hexanediol (**2a**) (Table I). When **1** was reacted with one equivalent of **2a** at room temperature for one day, colorless semi-solid was obtained in 94% yield after evaporating the solvent. Generally, boronic esters are known to be unstable toward moisture. The obtained oligomer in this study was also decomposed under air (*vide infra*). Due to this instability, the molecular weight could not be estimated exactly by means of GPC even upon nitrogen bubbling. Thus, the molecular weight of the obtained oligomer was measured by a cryoscopic method under nitrogen, and was found to be 600 (run 1).

Purification of the obtained oligomer was carried out by coagulation with *n*-pentane under nitrogen. As shown in runs 2 and 3 in Table I, the molecular weight of the *n*-pentane-soluble part (**3a**) was higher than that of *n*-pentane-insoluble part. This may be explained by assuming the contaminated low molecular weight oligomers with unreacted hydroxyl group at the end, which are more polar and are insoluble in *n*-pentane. The low molecular weight estimated by cryoscopy might be due to some impurities which are soluble in *n*-pentane.

Table I Polymerization Conditions.

Run	Diols	Conditions	Yield(%)	$\overline{M}_n$ a)
1	$HO(CH_2)_6OH$ (2a)	r.t. 1day	94	600
2			79 c)	1000
3			9 d)	210
4		reflux 4h	43 e)	1100
5		r.t. 1day b)	88 e)	1200
6	$HO(CH_2)_2OH$	r.t. 1day	-	150 (156 f))

a) From cryoscopy (dry 1,4-dioxane, under N_2). b) 15%excess thexyl borane was used for the reaction. c) *n*-Pentane-soluble part of run 1.
d) *n*-Pentane-insoluble part of run 1. e) *n*-Pentane-soluble part.
f) Calculated value for a cyclic compound.

From the IR spectrum of **3a**, the conversion of B-H group was found to be completed, while a small amount of unreacted hydroxyl group was observed. In its ^{1}H-NMR, however, the full characterization of the structure of **3a** was disturbed by its instability. Although a peak around 3.46-4.26ppm assignable to the protons of methylenes adjacent to boronic ester was observed, the integral ratio of protons of thexyl group to those of inner methylenes was somewhat lower (71%) than the calculated value for the expected structure. From this value, the molecular weight was calculated to be 640 by assuming that the terminal unit was derived from diol. When polymerization was carried out under THF reflux condition, the corresponding oligomer having the molecular weight of 1,100 was isolated in 43% yield (run 4). On the other hand, a small excess amount of **1** slightly improved the molecular weight of the oligomer (M_n=1,200, 88% yield, run 5).

Table II Dehydrogenation Polymerization of Various Diols.

Run	Diols	Conditions	Yield(%)	M.W.[a]
1	$HO(CH_2)_6OH$ (2a)	r.t. 1day	79[b]	1000
2	$HO(CH_2)_8OH$ (2b)	r.t. 1day	49[b]	1000
3	$HO(CH_2)_{12}OH$ (2c)	r.t. 1day	52[b]	1100
4	Hydroquinone (2d)	r.t. 1day	100[c]	-
5	Bisphenol A (2e)	r.t. 1day	56[b]	700

a) From cryoscopy (dry dioxane, under N_2). b) *n*-Pentane soluble part.
c) This polymer became insoluble during work up.

Various diols were subjected to this polymerization with an equimolar amount of **1** at room temperature (Table II). Diols such as 1,8-octanediol (**2b**), and 1,12-dodecanediol (**2c**), and also bisphenol A (**2e**) produced the corresponding oligomers like **2a**. The oligomer from **1** and hydroquinone (**2d**), however, became insoluble during the treatment with *n*-pentane.

The stability of **3a** against water was monitored by ^{1}H-NMR. When a $CDCl_3$ solution of **3a** was shaken with D_2O in a test tube at room temperature, the peak around 3.46-4.26ppm ($-CH_2-OB$) was found to be shifted to higher field (3.23-4.07ppm, $-CH_2-OD$)4). This result means that **3a** is readily decomposed by water, as is usual for boronic esters5).

Thermogravimetric analysis of **3a** was carried out under nitrogen stream or under air. As is shown in Figure 1, in both cases, the weight loss started at 100°C, and was completed at 480°C to give 8% of a residue.

The oligomers prepared in this study have low stability toward moisture. Nevertheless, unique characters and reactivities might be derived from the structures of boronic esters.

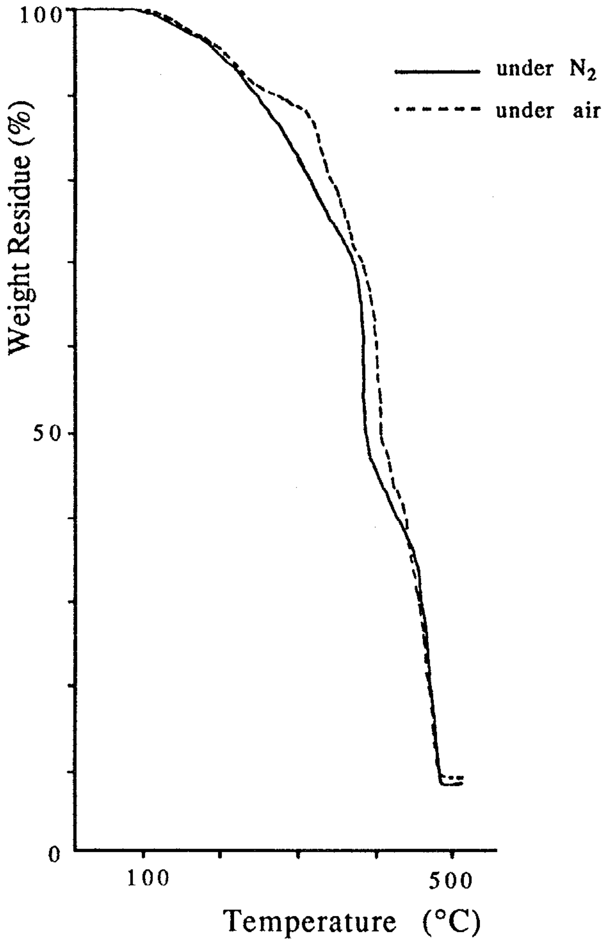


Figure 1 Thermogravimetric analysis of 3a.

Experimental Section

Materials and Instruments. **1** was prepared by the reaction of borane-THF complex and 2,3-dimethyl-2-butene[6) as reported earlier, and was purified by distillation[7) (48-49°C/0.1mmHg). Tetrahydrofuran and *n*-pentane were dried over lithium aluminum hydride and distilled before use. 1,4-Dioxane was dried over sodium and distilled before use. **2a**-**2c** were purified by distillation. **2d** and **2e** were recrystallized from benzene and from diethyl ether/ligroin, respectively.

^{1}H-NMR spectra were recorded in $CDCl_3$ on a Hitachi R-600 (60MHz) instrument. IR spectra were obtained on a Hitachi 260-50 spectrometer. Thermogravimetric analyses (TGA) were made on a Shimadzu DT-30 instrument (15°C/min.) under an air and a nitrogen stream. Cryoscopic experiments were carried out under nitrogen atmosphere using dried 1,4-dioxane as a solvent.

Synthesis of Boronate Oligomers (3a). As a typical procedure, to a 2.0M THF solution of **2a** (1.34g, 11.3mmol), **1** (1.11g, 11.3mmol) was added at ambient temperature under nitrogen atmosphere. The reaction mixture was kept standing at room temperature for 1 day under nitrogen. Evaporation of the solvent gave a colorless gum in 94% yield (2.26g, M_n=600, from cryoscopy). When the obtained gum was washed with three 10ml portions of *n*-pentane, 9% of white solid remained undissolved (M_n=210, from cryoscopy). The *n*-pentane-soluble part was collected and was freeze-dried with dry 1,4-dioxane to give 79% of **3a** as a semi-solid (M_n=1,000, from cryoscopy). ^{1}H-NMR (δ, ppm) 0.53-1.02 ($-CH_3$), 1.08-1.98 (-CH, $-CH_2-$), 3.86 ($O-CH_2-$, m); IR (neat) 2960, 1468, 1306, 1180, 1062cm^{-1}.

In a similar manner, **3b**-**3e** were prepared as follows: **3b** (from 0.296g, 3.02mmol of **1** and 0.438g, 3.00mmol of **2b**): Yield 0.353g (49%); ^{1}H-NMR (δ, ppm) 0.50-1.03 ($-CH_3$), 1.06-2.14 (-CH, $-CH_2-$), 3.86 ($O-CH_2-$, m); IR (neat) 2910, 1460, 1312, 1290, 1160, 1040cm^{-1}. **3c** (from 0.172g, 1.76mmol of **1** and 0.354g, 1.75mmol of **2c**): Yield 0.267g (52%); ^{1}H-NMR (δ, ppm) 0.53-1.03 ($-CH_3$), 1.06-2.18 (-CH, $-CH_2-$), 3.89 ($O-CH_2-$, m 4H); IR (neat) 2920, 1458, 1280, 1164, 1056cm^{-1}. **3d** (from 0.723g, 7.37mmol of **1** and 0.805g, 7.31mmol of **2d**, without treatment with *n*-pentane); ^{1}H-NMR (δ, ppm) 0.56-1.12 ($-CH_3$), 1.12-2.06 ($-CH_2-$), 6.38-7.02 (C_6H_4); IR (in $CHCl_3$) 2940, 1500, 1460, 1358, 1094, 900, 837cm^{-1}. **3e** (from 0.208g, 2.12mmol of **1** and 0.485g, 2.13mmol of **2e**): Yield 0.382g (56%); ^{1}H-NMR (δ, ppm) 0.50-1.08 ($-CH_3$), 1.08-2.04 (-CH, $-CH_2-$, $-CH_3$), 6.42-7.31 (C_6H_4, m); IR (in $CHCl_3$) 3320, 2950, 1604, 1460, 1355, 1080, 904cm^{-1}.

References and Notes

1) Teach, W. C. *Encyclopedia of Polymer Science and Technology,* **1965**, 2, 566.
2) Teach, W. C.; Green, J. *ibid.,* **1965**, 2, 581.
3) (a) Brown, H. C.; Gupta, S. K. *J. Am. Chem. Soc.,* **1971**, 93, 1816. (b) Brown, H. C.; Mandal, A. K.; Kulkarni, S. U. *J. Org. Chem.,* **1977**, 42, 1392. (c) Pelter, A.; Smith, K.; Brown, H. C. In *Borane Reagents*; Academic Press: London, 1988, p434 and references cited therein.
4) For example, $(EtO)_3B$ has a quartet peak at 3.83 ppm, while EtOH has the corresponding peak at 3.59 ppm.
5) Pelter, A.; Smith, K.; Brown, H. C. In *Borane Reagents*; Academic Press: London, 1988.
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7) See 2-1.

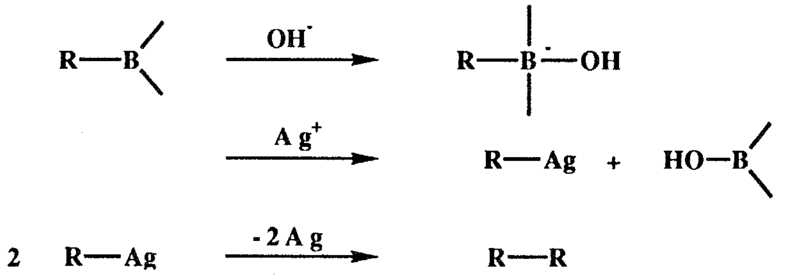
6 - 4

Ag(I)-Induced Coupling Polymerization of Bifunctional Organoboron Compounds.

Introduction

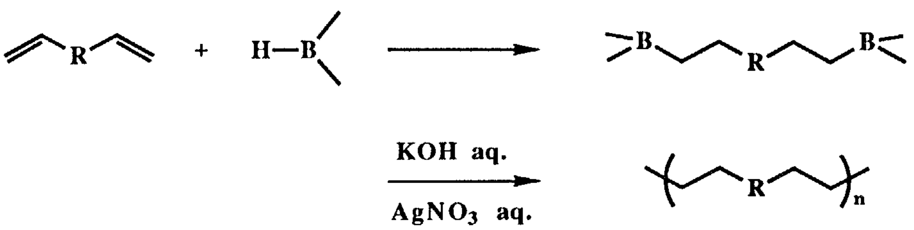
Homo-coupling reaction of organoboron compounds induced by silver nitrate has been used as an important synthetic tool for carbon-carbon bond formation in organic chemistry[1]. This reaction is believed to proceed *via* the migration of alkyl groups on a boron atom to silver, which breaks homolytically to form alkyl radicals[2]. These radicals formed here readily react each other to give a coupling product (Scheme I).

Scheme I



Bifunctional organoboron compounds prepared from dienes or internal acetylenes were subjected to this reaction to give cyclic hydrocarbons[3] or olefins[4], respectively. These reactions include the so-called intramolecular coupling. Consequently, if intermolecular coupling takes place, the formation of linear polymers can be expected. However, there have been very few examples of the polymerization via Ag(I)-induced coupling reaction of bifunctional organoboron compounds. Since the discovery of hydroboration method[5], organoboron compounds are readily available from the corresponding olefins. Thus, the expected bifunctional (telechelic) organoboron compounds can be prepared from dienes for the present study. The general idea of the present Ag(I)-induced coupling polymerization of telechelic organoboron compounds is shown in Scheme II.

Scheme II

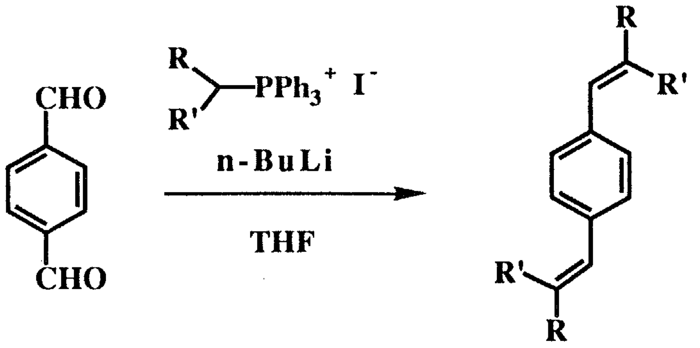


Results and Discussion

Bifunctional boranes were prepared from 1,7-octadiene[6] (**1a**) or *p*-divinylbenzene (**1b**) by the reaction with a large excess amount[7] of borane-tetrahydrofuran (BH_3/THF). However, these organoboron compounds gave only low molecular weight (several hundreds) oligomers after the reaction with silver(I) nitrate. From the results of the ^{1}H-NMR spectra of the oligomers obtained, the protons assignable to the terminal methyl groups were detected. The observed intensity of this peak was larger than that of the methyl groups of secondary borane species (6%)[5c], which were formed by the Markownikov addition of borane to C=C. This result must be caused by the disproportionation of two radicals formed. The coupling reaction of radicals is known to play an important role as a termination in radical polymerization. Thus, in the present system, it seems to be important to increase the proportion of recombination of two radicals to avoid undesirable disproportionation.

It is well-known that the recombination mainly takes place as a termination in the radical polymerization of styrene[8]. Accordingly, if starting dienes can be designed as to favor the formation of benzylic borane at the hydroboration stage, the following coupling polymerization comes closer to the model of termination of radical polymerization system of styrene. For this purpose, *β,β'*-dimethyl-*p*-divinylbenzene (**1c**) and *β,β,β',β'*-tetramethyl-*p*-divinylbenzene (**1d**) were prepared respectively by the Wittig reaction of terephthalaldehyde with the corresponding phosphonium salts (Scheme III), and were examined for the present coupling polymerization.

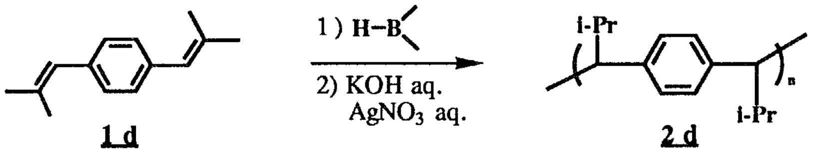
Scheme III

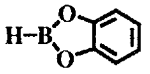


1c; R=Me R'=H
(*cis*, *trans* mixture)

1d; R=R'=Me

Table I Ag(I)-Induced Coupling Polymerization of **1d** Using Various Boranes.



Run	Borane	2d Yield (%)$^{a)}$	$\overline{M}_n$$^{b)}$	$\overline{M}_w$$^{b)}$
1	BH_3/THF	63	2,630	5,880
2	$Me_2S \cdot BH_2Br$	81	42,200	116,500
3		63	800	1,060
4	9-BBN	-	1,360	2,770

a) Isolated yields after reprecipitation into MeOH.
b) GPC (THF), polystyrene standard.

When **1d** was reacted with various kinds of boranes followed by the treatment with silver(I) nitrate under alkaline conditions, the molecular weights of the resulting polymers were quite dependent on the boranes used (Table I). Monobromoborane-dimethyl sulfide$^{9)}$ ($Me_2S \cdot BH_2Br$) was reported to be more selective hydroboration reagent in comparison with BH_3/THF. Higher selectivity in hydroboration increased the ratio of benzylic borane species, which is more suitable for the present coupling polymerization. When catecholborane or 9-borabicyclo[3.3.1]-nonane (9-BBN) was used at the hydroboration stage, the resulting polymers had rather low molecular weights (runs 3 and 4). In the case of catecholborane, the dimethyl substituent in **1d** seems to be too large for the complete hydroboration[10]. 9-BBN also did not give high molecular weight polymers because the bicyclic alkyl group in 9-BBN also produced radicals, which interrupted the desired polymerization[11].

Among the boranes examined here, $Me_2S \cdot BH_2Br$ was found to be the best hydroboration reagent. Thus, regioselectivity of hydroboration reaction was examined using $Me_2S \cdot BH_2Br$ with a model compound (β,β-dimethylstyrene, **3d**). As depicted in Scheme IV, the boron atom was favorably introduced at the benzylic position (87%) by using **3d**, which possessed a dimethyl substituent at the β-position[12]. It should be noted here that even the unfavorable organoboron species (13% boron at β-position) might cause mainly the coupling reaction because the radical formed in this case should be tertiary one.

Scheme IV

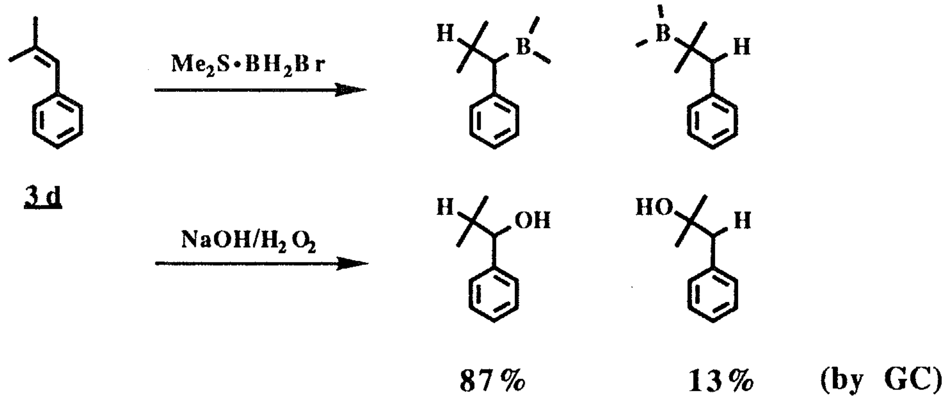
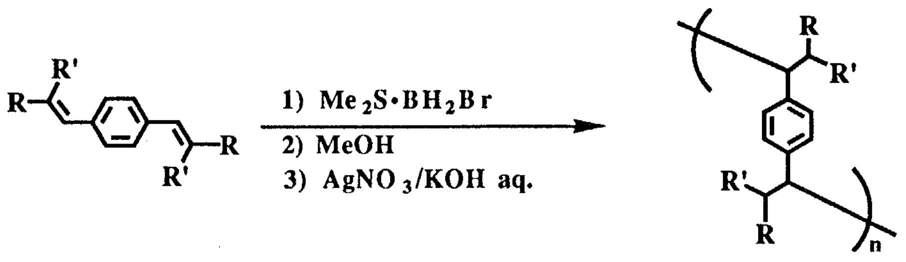


Table II summarizes the results of Ag(I)-induced coupling polymerization starting from **1b**-**1d**. The more substituents at the β-position of diolefins, the higher molecular weights polymers were obtained. This result supports the idea that recombination of radicals should be important in the present Ag(I)-induced coupling polymerization.

Table II Ag(I)-Induced Coupling Polymerization of Various Diolefins Using $Me_2S{\bullet}BH_2Br$.



1 2

Run	Compounds	R	R'	Yield (%)[a]	$\overline{M}_n$[b]	$\overline{M}_w$[b]
1	1b	H	H	-	360	840
2	1c	Me	H	47	6,330	27,600
3	1d	Me	Me	81	42,200	116,500

a) Isolated yields after reprecipitation into MeOH.
b) GPC (THF), polystyrene standard.

Experimental Section

Materials and Instruments. 1b, 1c, and benzaldehyde were distilled before use. BH_3/THF and $Me_2S{\bullet}BH_2Br/CH_2Cl_2$ (1.0M) were obtained from Aldrich and were used without purification. All the solvents for hydroboration reaction were dried and distilled before use. Alkyl halides, isophthalaldehyde, terephthalaldehyde, potassium hydroxide, sodium chloride, diethyl ether, *n*-hexane, ethanol, and silver nitrate were used as received.

^{1}H-NMR spectra were recorded in $CDCl_3$ on a Hitachi R-600 instrument. ^{13}C-NMR spectrum was recorded in $CDCl_3$ on a JEOL JNM-JX-400 instrument. IR spectra were obtained on a Perkin Elmer 1600 spectrometer. Gas chromatographic analysis (GC) was made on a Shimadzu GC-6A instrument. Gel permeation chromatographic analyses were carried out on a Tosoh HLC-8020 (TSK gel G3000, or G4000) by using THF as an eluent after calibration with standard polystyrene samples.

Synthesis of Monomers. *β,β'*-Dimethyl-*p*-divinylbenzene (1c), *β,β,β',β'*-tetramethyl-*p*-divinylbenzene (1d),

and β,β-dimethylstyrene (3). To a THF (200ml) solution of ethyltriphenylphosphonium iodide (16.8g, 40.2mmol), *n*-butyllithium (1.68N in *n*-hexane, 23.8ml, 40mmol) was added dropwise, and the resulting mixture was stirred for 30 min. at room temperature. To the generated phosphonium ylide, terephthalaldehyde (2.65g, 19.8mmol) in 20ml of THF was added from a dropping funnel and the mixture was kept stirring for 1 day. The obtained reaction mixture was evaporated and was washed with *n*-hexane for 5 times (in total, 100ml). The *n*-hexane solution thus obtained was evaporated and distilled under reduced pressure (80-82°C/0.5mmHg) to give pure **1c**. **1c**; 1.89g (60% yield); ^{1}H-NMR (δ, ppm) 1.66-2.03 (d, 6H), 5.52-6.69 (m, 4H), 7.24 (s, 4H).

In a manner similar to this, **1d** and **3** were prepared. **1d** (from *i*-propyltriphenylphosphonium iodide, *n*-butyllithium, and terephthalaldehyde): bp 94°C/0.1mmHg; ^{1}H-NMR (δ, ppm) 1.86 (s, 12H), 6.24 (s, 2H), 7.18 (s, 4H); IR (neat) 3070, 3019, 2910, 2850, 1502, 1371, 1104, 1055, 870cm^{-1}. **3** (from *i*-propyltriphenylphosphonium iodide (21.5g, 50mmol), *n*-butyllithium (1.7N in *n*-hexane, 33.2ml, 50mmol), and benzaldehyde (4.5g, 42mmol)): 77% yield; (bp 69-72°C/15mmHg); ^{1}H-NMR (δ, ppm) 2.19 (s, 6H), 6.63 (s, 1H), 7.57 (s, 5H).

Coupling Polymerization of 1d. As a typical procedure, a coupling polymerization of bifunctional organoboron compound prepared from **1d** and $Me_2S{\bullet}BH_2Br$ is described as follows: To a two-way flask equipped with a stirrer tip, a septum inlet, and a three-way cock, **1d** (0.093g, 0.5mmol) and $Me_2S{\bullet}BH_2Br$ (1.0M in CH_2Cl_2, 5.0ml, 5mmol) were added at 0°C under nitrogen. After several hours at ambient temperature, methanol (1.0ml) was added slowly and the reaction mixture was concentrated under reduced pressure. The obtained material was further reacted with $Me_2S{\bullet}BH_2Br$ (1.0M in CH_2Cl_2, 5.0ml, 5mmol) for 1 day and was treated again with methanol (1.0ml). After the removal of volatile fractions under reduced pressure, THF (5.0ml) was added, and the solution was treated with aqueous potassium hydroxide (5.0N, 2.5ml), and silver nitrate (5.0N, 1.5ml) at 0°C for 2h. The resulting suspension was treated with saturated aqueous sodium chloride and was filtered. The obtained solution was extracted with benzene and was concentrated. The polymer thus obtained was purified by the precipitation with methanol. **2d**: 0.075g (81% yield); ^{1}H-NMR (δ, ppm) 0.35-1.20 (m, 12H), 1.45-2.25 (br, 2H), 4.15-4.75 (m, 2H), 7.00-7.50 (m, 4H); ^{13}C-NMR (δ, ppm) 19.3, 19.4, 32.2, 90.0, 91.1, 125.5, 127.0, 140.0, 140.3; **IR** (film) 2954, 1589, 1463, 1093, 1017, 804 cm^{-1}.

Oxidation of Organoboron Compound Prepared from 3. Similarly to the polymerization reaction described above, hydroboration of **3** (0.171g) was carried out with excess amount of $Me_2S \cdot BH_2Br$ (1.0M, 3ml), which was oxidized in THF (5ml) with aqueous sodium hydroxide (6N, 5ml) and hydrogen peroxide (30%, 4ml) at 50°C for 2h. The resulting alcohols were subjected to GC measurement on the basis of the authentic samples prepared from acetone with benzylmagnesium chloride, and benzaldehyde with *i*-propylmagnesium bromide, respectively.

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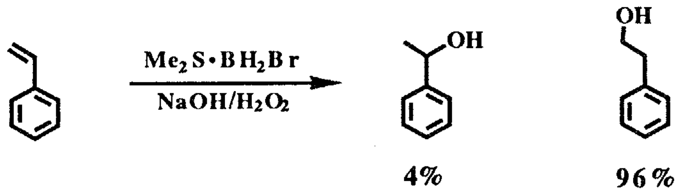
12) In the case of styrene, hydroboration reaction with $Me_2S{\bullet}BH_2Br$ is reported to form benzylic borane only in 4% selectivity as shown in the following scheme;



Chapter 7

Summary

SUMMARY

This thesis has dealt with the syntheses of novel organoboron polymers, several reactions of the resulting organoboron polymers to show the unique reactivity of these polymers as the precursors for functional polymers, syntheses of novel boron-containing polymers bearing boron-nitrogen four-membered structures in the main chain, and other methods providing boron-containing materials.

Hydroboration polymerization of thexylborane with dienes or diynes gave novel organoboron polymers that contained organoboron repeating units in the main chain. The organoboron polymers obtained were rather unstable to be decomposed when exposed under air (Chapter 2).

However, these polymers showed quite unique reactivities for the production of various organic polymers by the polymer reactions accompanying the rearrangement of the main chains (Chapter 3). Among the enormous studies of polymer reactions, very few works have been dealt with reactions including the rearrangement of the main chain. Using this novel polymer synthetic methodology, various functional polymers may be designed and synthesized.

Boron-containing polymers obtained by the hydroboration polymerization of dicyano monomers were quite stable to be kept under air (Chapter 4). These boron-containing polymers gave some residue after the pyrolysis that may open a useful way to obtain boron-containing inorganic materials.

Boron-containing polymers with the similar structure consisting of B-N four-membered rings could be also prepared by allylboration reactions between allylboranes and dicyano compounds (Chapter 5). The stability of boron-containing polymers depended on the substituents on the boron atoms in the polymer. For the alternative method to obtain boron-containing polymers with similar structures, condensation reactions of bis(silylimine)s with chlorodialkylboranes were also examined. Similarly to the polymers prepared by the hydroboration polymerization of dicyano monomers, these polymers also gave some residue after pyrolysis.

Further studies related to the previous chapters of this thesis, haloboration polymerization of diynes, hydroboration reaction of double bond-terminated polymers, dehydrogenation polymerization of monoalkylborane with diols, and a coupling polymerization of bifunctional organoboron compounds mediated with silver(I) have been described in Chapter 6. Especially, poly(organoboron halide)s prepared by haloboration technique showed novel properties as Lewis acids that have been hardly investigated before.

The organoboron polymers and boron-containing polymers prepared in the present thesis may be expected as new polymeric materials having characteristic properties. In addition, the organoboron polymers can be used as polymeric precursors that can be converted to various functional polymers. In other words, a wide variety of functional groups can be introduced at the main chains, side chains, terminal ends, or even at the center of polymeric chains starting from these organoboron polymers. The present methodology seems to have a high potential to provide functional polymers that are difficult to prepare by the known polymer synthetic methods. The author hopes that the methods presented here may be extended and utilized in the future for the preparation of structurally controlled polymers as well as novel materials with unique properties.

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