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

Substituted boron halides are useful reagents for ether cleavage[1] and selective haloboration reactions[2] 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.

Very recently, we reported hydroboration polymerization, in which novel organoboron polymers were prepared by polyaddition between monoalkylborane and diene compounds.[3] The resulting organoboron polymers were demonstrated as reactive polymers by the reaction with carbon monoxide or with potassium cyanide to produce polyalcohol or polyketone, respectively.[4] Here we report a polyaddition between boron tribromide and terminal diynes as a novel methodology for the preparation of poly(organoboron halide)s. We propose to term this polymerization "haloboration polymerization" (Scheme I).

Haloboration reaction is beginning to be known to provide key intermediates for the synthesis of substituted olefins.[5] This reaction proceeds chemoselectively and stereoselectively under the appropriate reaction conditions.[6] The reactivity of a boron-halide moiety toward 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 makes possible the formation of a linear polymer without gelation by supplying two B-Br bonds from boron tribromide. Thus, as a typical and preliminary example, haloboration polymerization between boron tribromide (**1**) and 1,7-octadiyne (**2**) is described here. 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.

Polymerization was carried out by adding an equimolar amount of **2** to a 1 M 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 **2** was quantitative. After coagulation with dry *n*-pentane under nitrogen, the polymer **3** was isolated as a brown solid in 90% yield. The structure of the obtained polymer **3** was supported by spectroscopic analyses. Figure 1 represents the ^1H NMR spectrum of **3**, 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.

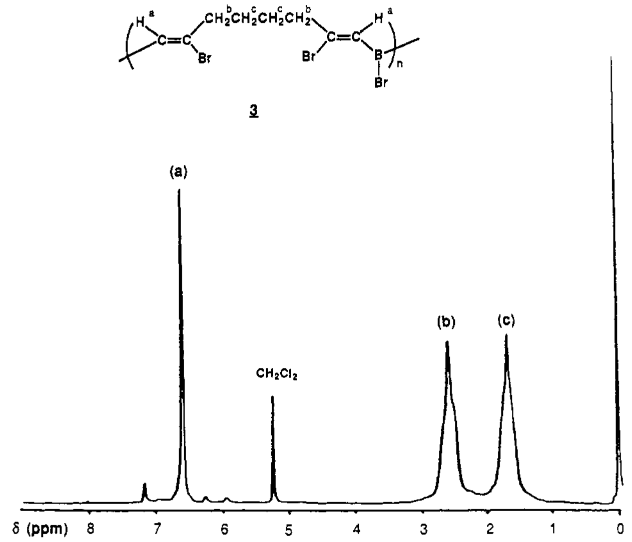
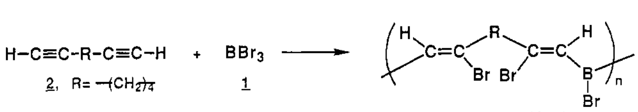


Figure 1. ^1H NMR spectrum of organoboron polymer **3** prepared from BBr_3 and 1,7-octadiyne.

Scheme I



Judging from the previous report of Blackborow,[6] the chemical shift of the vinyl protons (δ 6.69) indicates a *Z* structure of **3** (vide infra). In its IR spectrum, the strong peak at 1580 cm^{-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 **3** was measured by GPC ($CHCl_3$ as an eluent)

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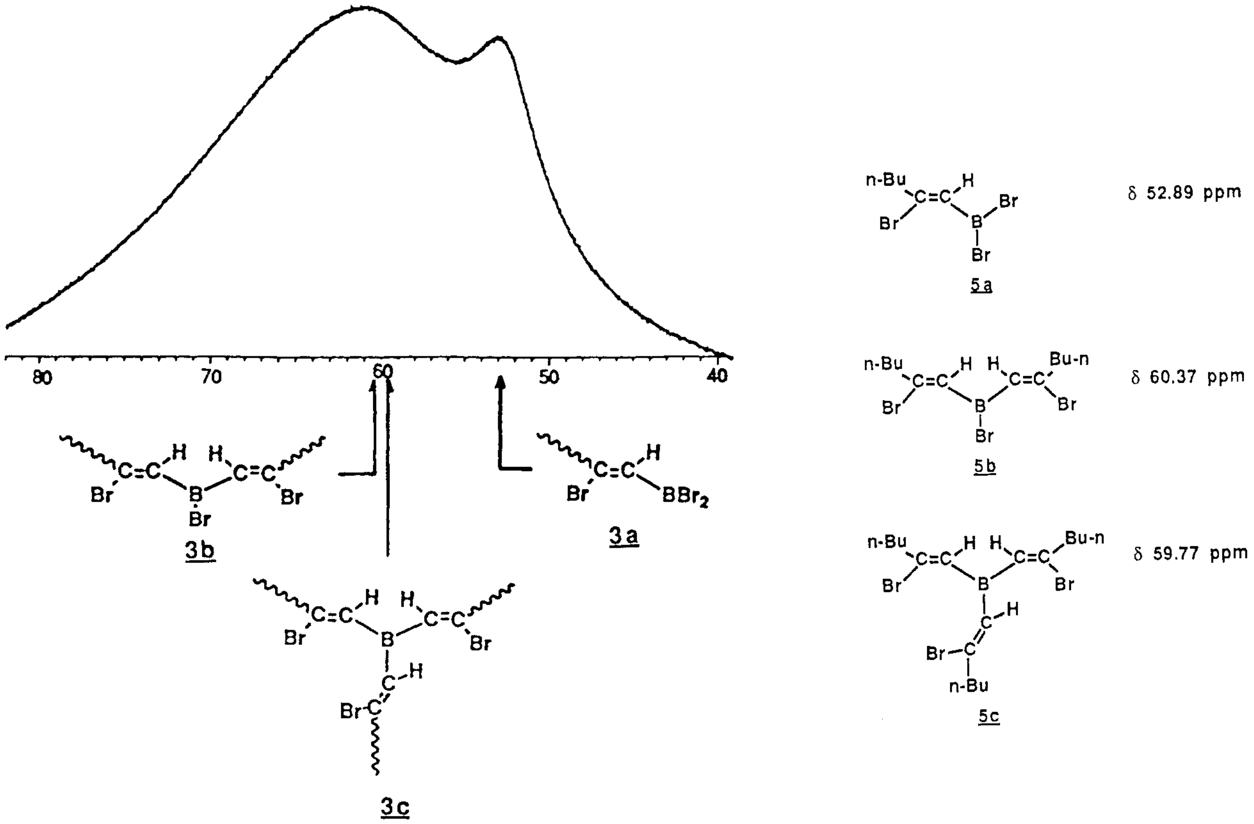
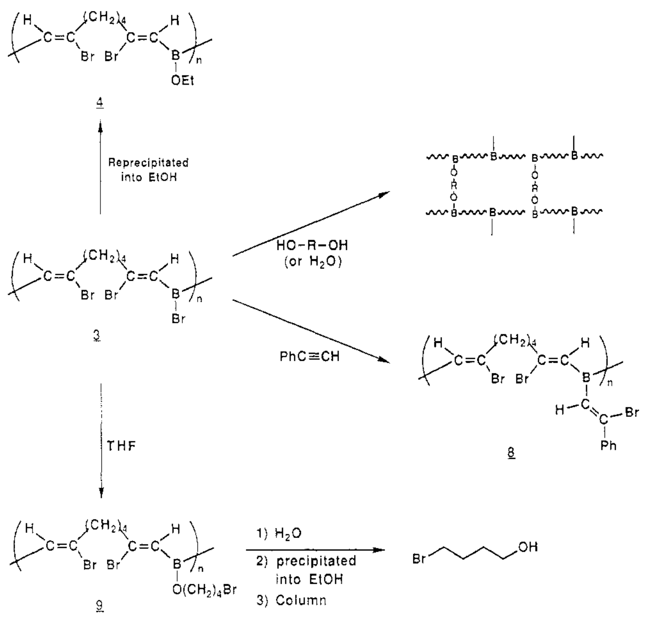
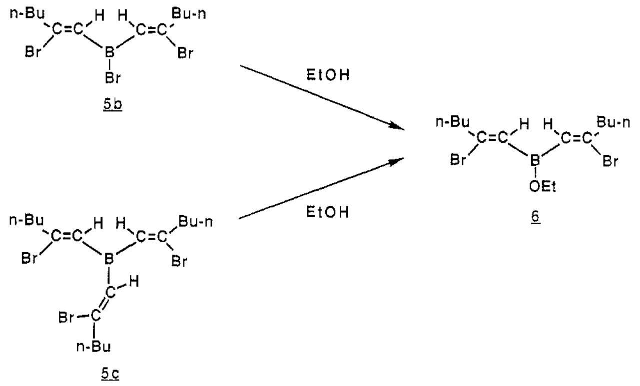


Figure 2. ^{11}B NMR spectrum of 3.

Scheme II



Scheme III



using polystyrene calibration curves, from which $\bar{M}_n$ and $\bar{M}_w$ were found to be 5200 and 17 000, respectively. After the measurement of GPC, however, the structure of the polymer was proven to be changed into 4 from its ^{1}H NMR analysis. That is, the B–Br moiety was replaced by B–OEt.[5,7,8] This result may be explained by the reaction of 3 with a small amount of ethanol, which usually contaminates $CHCl_3$ as a stabilizer. This replacing reaction was also observed when 3 was precipitated into ethanol (Scheme II), in which 4 was obtained in 93% yield.[9] Thus, 3 and 4 were found to indicate eventually the same molecular weight in GPC measurement.

^{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 (**5a**–**5c**)[6] were prepared as models for the corresponding polymer structures (**3a**–**3c**), respectively. As illustrated in Figure 2, **5a** (polymer-end model), **5b** (main-chain model), and **5c** (branched-structure model) showed resonances at δ 52.9, 60.4, and 59.8, respectively. On the other hand, the polymer **3** showed a resonance at δ 60.8 accompanying a shoulder peak at δ 52.9. Thus, the former (main) peak of **3** 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 **3** 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 (**3c**) in the polymer. It should also be noted that no gelation was observed during haloboration polymerization.

Table I
Dependence of Molecular Weight on the Feed Ratio of Diyne/BBr_3[a]

run	BBr_3, g (mmol)	diyne, g (mmol)	diyne/BBr_3 ratio	molec wt[b]
1	0.320 (1.28)	0.102 (0.96)	0.75	830
2	0.278 (1.11)	0.100 (0.94)	0.85	3320
3	0.423 (1.69)	0.169 (1.59)	0.94	6420
4	0.526 (2.10)	0.225 (2.11)	1.00	15500
5	0.403 (1.61)	0.178 (1.67)	1.04	28000
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 room temperature. [b] GPC ($CHCl_3$, PSt standard), peak top molecular weight. [c] Gelation was observed when the system was warmed up to 0 °C.

From either **5b** or **5c**, the same product (**6**) was afforded by the reaction with ethanol (Scheme III). This result indicates that one B–C bond in trialkenylborane (**5c**) is reactive to ethanol to form B–OEt similarly to B–Br in **5b**. Accordingly, if the polymer **3** has a branched structure of the trialkenylborane moiety (**3c**) 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 **3** was further confirmed by UV measurement. The polymer **3** and its model compound (**5b**) showed the same absorption maximum at 255 nm, which is assignable to the $C{=}C{-}B{-}C{=}C$ moiety. By using a molar absorptivity for **5b**, this structure was proven to exist almost quantitatively in **3**. To elucidate the stereochemistry of haloboration polymerization, acid hydrolysis of **3** 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 ^1H NMR analysis, more than 77% of **7** was proven to contain the *Z* isomer. This result is taken to mean that the present haloboration polymerization proceeds mainly in cis addition of boron bromide to terminal acetylene.

The results of haloboration polymerization between **1** and **2** by changing the feed ratio of **2** to **1** are summarized in Table I. The molecular weight of the obtained polymer was increased when the ratio of **2** to **1** 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 treatment with ethanol. The soluble product showed lower molecular weight (GPC, $\bar{M}_n = 4100$, $\bar{M}_w = 12\,100$) 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.

The reactivity of B–Br in **3** was demonstrated as follows. Terminal monoyne compounds such as phenylacetylene were added to a dichloromethane solution of **3**. In this reaction, a further haloboration occurred to produce **8** as shown in Scheme II. The formation of **8** was supported by its ^1H NMR spectrum,[10] although **8** was decomposed during GPC measurement.

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

3 was also subjected to the ether cleavage reaction. For example, when excess THF was introduced into a dichloromethane solution of **3** at 0 °C, the polymer structure was found to be changed into **9** (Scheme II) by its ^1H NMR.[11] After hydrolysis of **9**, followed by the purification with SiO_2 column chromatography, 4-bromo-1-butanol was isolated in 90% yield based on **3**. This reaction also demonstrates the characteristic property of **3** as a poly(Lewis acid).

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(9) **4**: ^1H NMR ($CDCl_3$) δ 1.27 (CH_3CO-, t, 3 H), 1.62 ($-CH_2CC{=}C$, m, 4 H), 2.54 ($-CH_2C{=}C$, m, 4 H), 4.09 ($-OCH_2-$, q, 2 H), 6.24 ($C{=}CHB$, 2 H).
(10) **8**: ^1H NMR ($CDCl_3$) δ 1.68 ($-CH_2CC{=}C$, m, 4 H), 2.60 ($-CH_2C{=}C$, m, 4 H), 6.59–7.05 ($-CCBr{=}CH-$, 2 H), 7.10–7.92 ($C_6H_5CBr{=}CH-$, m, 6 H).
(11) **9**: ^1H NMR ($CDCl_3$) δ 1.62 ($-CH_2CC{=}C$, m, 4 H), 1.84 ($-OCCH_2CH_2CBr$, m, 4 H), 2.54 ($-CH_2C{=}C$, m, 4 H), 3.47 ($-CH_2Br$, t, 2 H), 4.07 ($-CH_2OB$, t, 2 H), 6.24 ($C{=}CHB$, 2 H).

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Pyrene as a Fluorescent Probe for Monitoring Polymerization Rates

During the past few years monitoring of polymerization reactions using fluorescent probes has been the subject of numerous investigations. Changes in fluorescence yields,[2-6] polarization,[3,7] diffusion coefficient,[8] and the efficiency of intramolecular excimer formation[9-11] have been related to the changes in viscosity that occur during the polymerization event and, as such, are used in particular to monitor the extent of cure in certain applications.

An excimer (*exci*ted di*mer*) is formed by the diffusion-controlled reaction between a molecule in the excited state and another in the ground state and is characterized by a broad, structureless emission red-shifted with respect to the fluorescence emission of the monomer.[12] Provided that only two excited states are involved, the ratio of pyrene monomer to excimer emission is a linear function of the medium viscosity.

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