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Hydroboration copolymerization

Synthesis of organoboron copolymers by the reactions of dienes or diene/diyne with thexylborane

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Summary

Organoboron copolymers were prepared by polyaddition of diene mixture or diene/diyne mixture, respectively, with thexylborane (**1**). When a mixture of dienes such as 1,2-diallyloxyethane (**2a**) and *p*-diallylbenzene (**2b**) was polymerized with **1**, the peaks in GPC using both UV and RI detectors were shifted to higher molecular weight regions with the increase of the amount of **1**. The molecular weight distribution of the copolymer obtained by this method indicated clear difference from that of a mixture of two homopolymers. On the other hand, when the poymerization between **1** and 1,7-octadiene (**2c**) was carried out in the presence of a trace amount of 1,7-octadiyne (**4**), the molecular weights of organoboron polymers were found to be increased when the ratio of **4**/**2c** was increased.

Introduction

Recently, we have reported the synthesis of organoboron polymers by polyaddition of thexylborane with dienes (3) or with diynes (4) (i.e., Hydroboration Polymerization, Scheme I). The obtained polymers can be regarded as a polymer homologue of trialkylboranes, which are very versatile reagents for the preparation of a wide variety of functional compounds in organic synthesis (5). Similarly, the organoboron polymers prepared by hydroboration polymerization could be successfully used as reactive polymeric materials to give other polymers having functional groups. For example, the reaction of organoboron polymer with carbon monoxide, cyanide anion, or with dichloromethyl methyl ether gave poly(alcohol) (6), poly(ketone) (7), or poly(alcohol) (8), respectively (Scheme II). 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.

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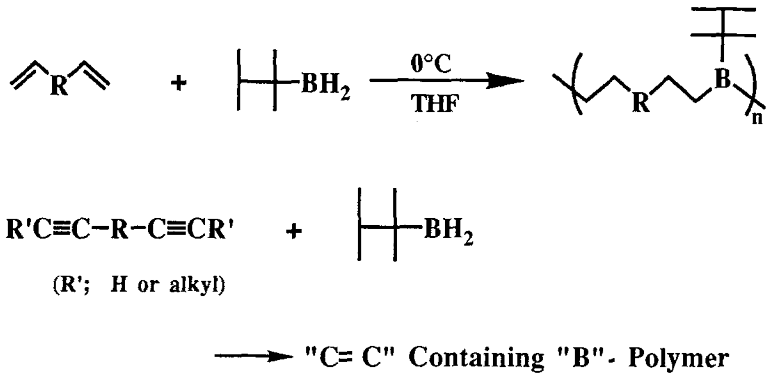
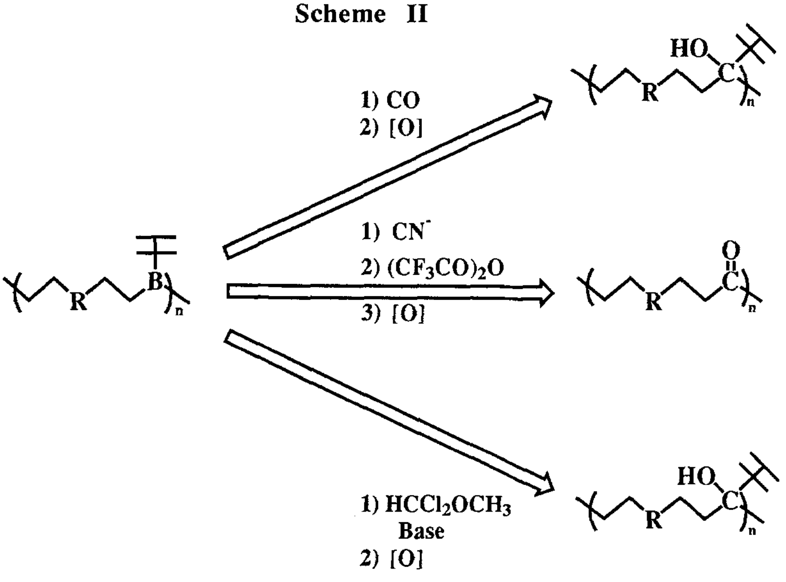
[1,2] See reference list

Scheme I



Scheme II

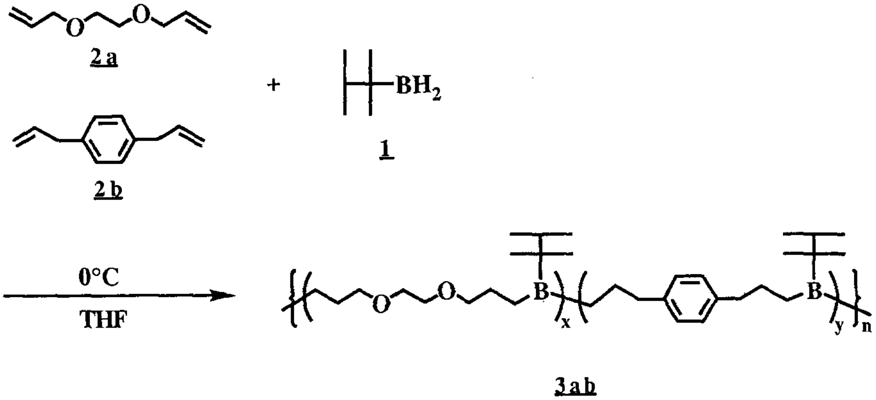


Results and Discussion

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 atom towards boron in the main chains. On the other hand, polymerization of p-diallylbenzene (**2b**) gives the corresponding high molecular weight polymer, which has strong UV absorption (3). 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** (at 1:1 molar ratio) with various amounts of **1** were examined (Scheme III). The molecular weights of polymers obtained here (**3ab**) were estimated directly by GPC measurements (dried THF as an eluent, polystyrene standards) (Figure 1). In all cases, the peaks in GPC detected by UV had quite similar shapes to those detected by RI. The molecular weights of polymers (**3ab**) reached to 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 dienes (3). ^{1}H-NMR and IR spectra of the polymers thus obtained were consistent with the structure of the expected copolymers.

Scheme III



The formation of copolymer by the present method was further confirmed by the comparison of GPC measurement with a mixture of two homopolymers of **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** homopolymer, whereas the corresponding peaks by RI were the sum of those of **3a** and **3b**. In other words, no specific interaction between these two polymers was observed in GPC measurement. These results clearly show the formation of the corresponding copolymer in Figure 1. M_n and M_w of the obtained copolymer (**3ab**) were 2,340 and 6,400, respectively. These values were in a similar range of those of two 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).

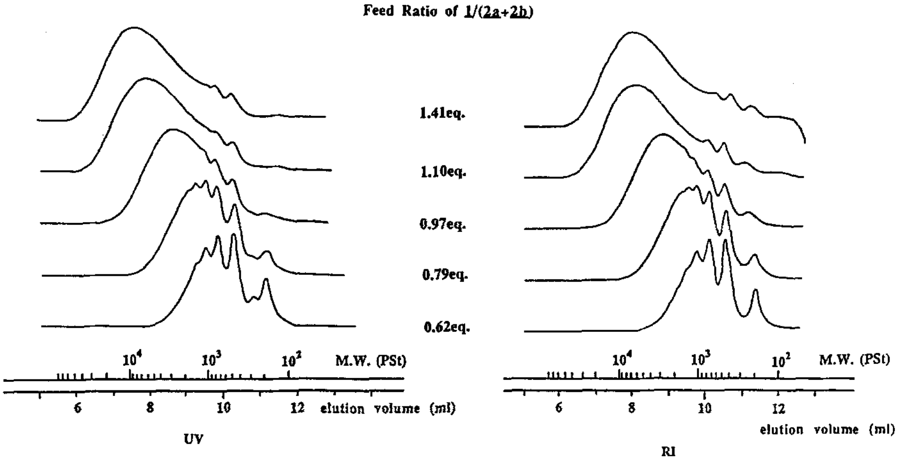
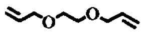
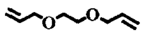
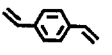
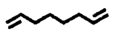
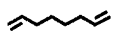


Figure 1. GPC traces of hydroboration copolymerization of **1** and **2a**/**2b**.

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 diyne gives organoboron polymer having branched structure due to the further hydroboration reaction towards the initially formed vinylborane structures (4). That is, terminal diynes are taken to have a potential

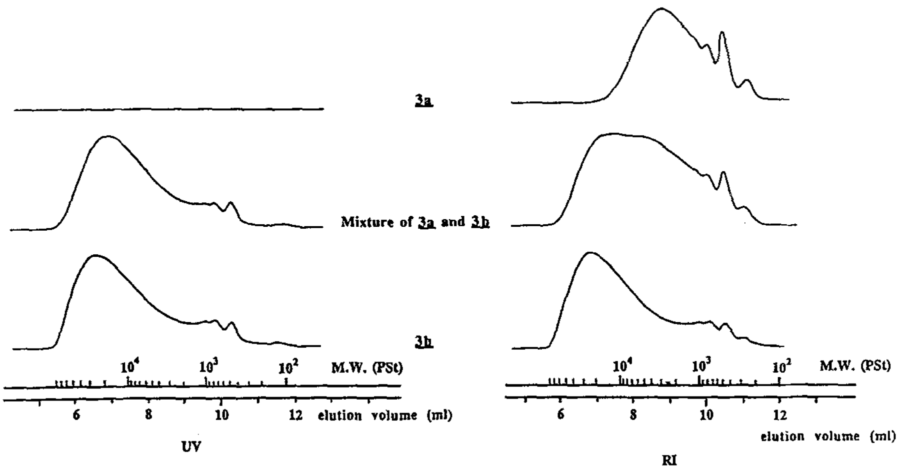


Figure 2. GPC traces of **3a**, **3b**, and a mixture of **3a** and **3b**.

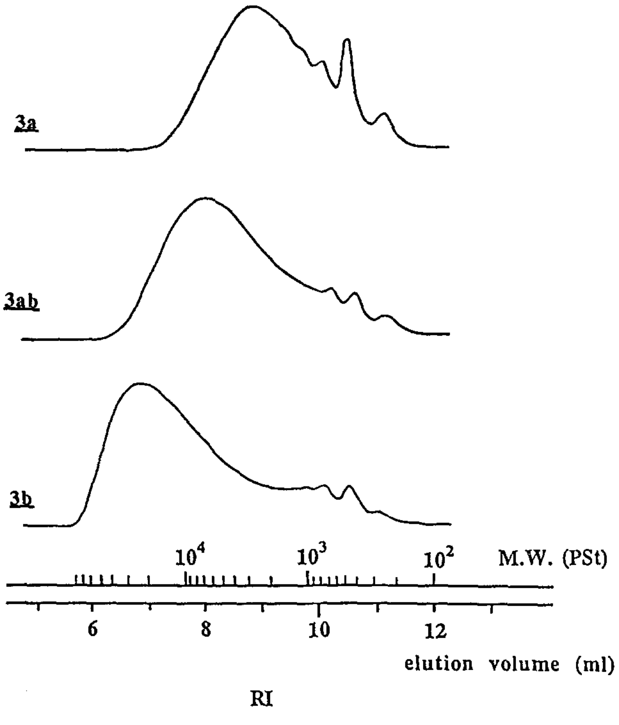
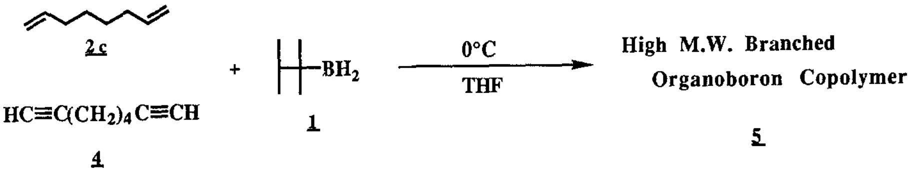


Figure 3. GPC traces of **3a**, **3ab**, and **3b**.

as a multifunctional monomer. Thus, hydroboration polymerization between 1,7-octadiene (**2c**) and **1** was examined in the presence of a small amount (0-5 molar % to **2c**) of 1,7-octadiyne (**4**) (Scheme IV).

Scheme IV



All reactions were carried out by adding a small excess amount 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**. When 5 molar % of **4** was used, 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 (9). As a result, GPC measurement was carried out after methanolysis (run 3). Although the number average molecular weight of copolymer (**5**) prepared by this method was comparable to that of homopolymer (**3c**), the weight average molecular weight was considerably increased (run 1 vs run 2). This copolymerization method using diyne may provide a synthetic route to obtain higher molecular weight (including gels) organoboron polymers.

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

Run	Diene (mmol)	Diyne (mmol)	Molar ratio	$\bar{M}_n$[b]	$\bar{M}_w$[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.

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% to dienes) was added by using a microfeeder (45μmol/min.) at 0°C under nitrogen. This reaction mixture was kept stirring for an additional 1 hour, and was subjected to GPC measurement directly. To this reaction mixture, 0.027g, 0.029g, 0.021g, and then 0.049g (total 1.27mmol) of **1** was added successively using a microfeeder (45μmol/min.) at 0°C under nitrogen. After the completion of each feeding, the reaction mixture was kept stirring for 1 hour, and was subjected to GPC measurement directly.

Synthesis of Organoboron Copolymers (3ad, 3bc, 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** (0.1284g, 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 minutes, gelation was observed. GPC was measured after dissolving this gel by the treatment with methanol (0.2ml). Similarly, 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 5 hours.

References and Notes

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2. Present address: KRI International, Inc., Kyoto Research Park, 17, Chudoji, Minami-machi, Shimogyo-ku, Kyoto 600, Japan
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9 As discussed in ref (4), gem-diboramethylene should be cleaved easily under protic conditions.

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