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Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

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To cite this Article Chujo, Yoshiki(1994) 'Versatile Reactions of Organoboron Polymers Prepared by Hydroboration Polymerization', Journal of Macromolecular Science, Part A, 31: 11, 1647 – 1655

To link to this Article: DOI: 10.1080/10601329408545874

URL: <http://dx.doi.org/10.1080/10601329408545874>

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VERSATILE REACTIONS OF ORGANOBORON POLYMERS PREPARED BY HYDROBORATION POLYMERIZATION

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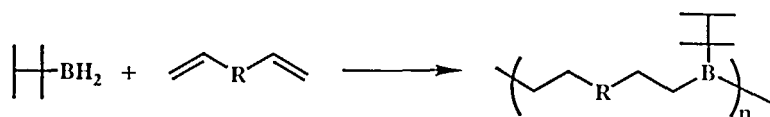
ABSTRACT

Hydroboration polymerization of dienes and thexylborane produces organoboron polymers, which can be regarded as a polymer homolog of trialkylboranes. In other words, the organoboron polymers obtained can be expected to be a novel type of reactive polymer. The present paper describes versatile reactions of organoboron polymers prepared by hydroboration polymerization. For example, reactions with carbon monoxide or with KCN were followed by oxidative treatment to produce the corresponding poly(alcohol)s or poly(ketone)s, respectively. The organoboron polymers were also reacted with bromopyridyl anion or with furyl anion to form cyano- or hydroxyl-containing polymers via ring-opening of pyridine or furan, respectively. Reductive treatment of the organoboron polymer gave the corresponding polymer after reductive cleavage of carbon—boron bonds.

INTRODUCTION

Recently, we explored “hydroboration polymerization” (Scheme 1) as a novel methodology for the preparation of organoboron polymers [1–3]. This polymerization can be applied to various combinations of dienes with thexylborane to produce the corresponding organoboron polymers as summarized in Table 1.

The polymers prepared by hydroboration polymerization have a new structure



SCHEME 1.

consisting of carbon—boron bonds in the main chain, and they can be regarded as a polymer homolog of trialkylboranes. Generally, trialkylboranes are very useful reagents for the preparation of a wide variety of functional compounds. This chemistry has been mainly explored by Brown and his group [4, 5]. Accordingly, the polymers obtained by hydroboration polymerization can be expected to be a novel type of reactive polymers. We describe here the versatile reactions of organoboron polymers as demonstrated in Scheme 2.

REACTIONS OF ORGANOBORON POLYMERS WITH CARBON MONOXIDE TO POLYALCOHOLS

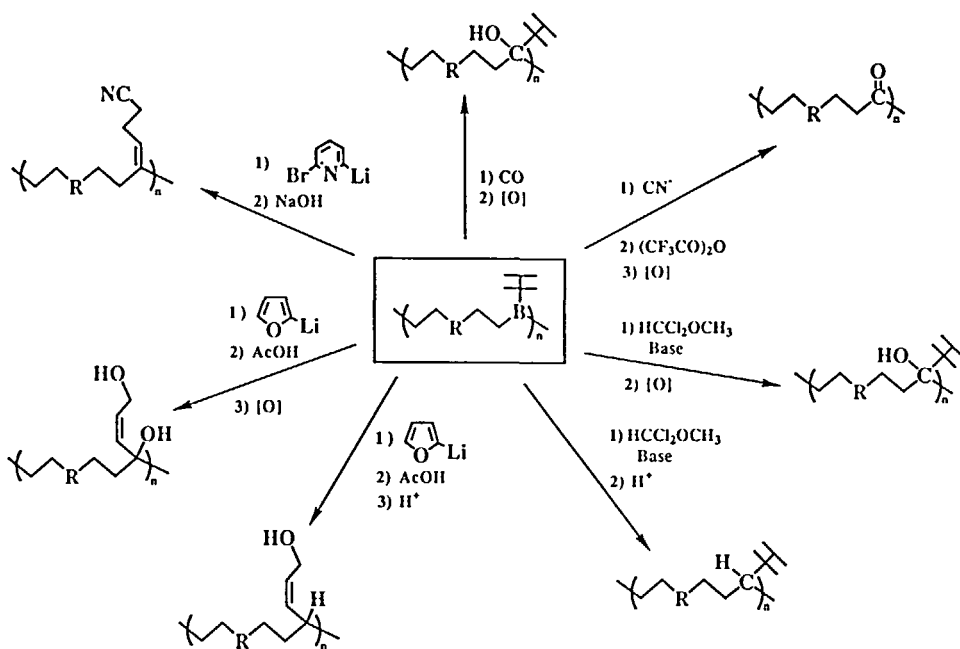
The polymer prepared from thexylborane and 1,7-octadiene was reacted with carbon monoxide at 120°C, followed by treatment with NaOH and H₂O₂ to produce

TABLE 1. Hydroboration Polymerization between Thexylborane and Various Dienes^a

Run	Diene	\bar{M}_n^b	\bar{M}_w^b
1		19,000	27,700
2		18,400	27,400
3		19,000	29,200
4		9,400	16,900
5		1,200	2,600
6		1,900	4,500
7		1,900	3,200
8		5,100	11,200
9		7,600	15,400

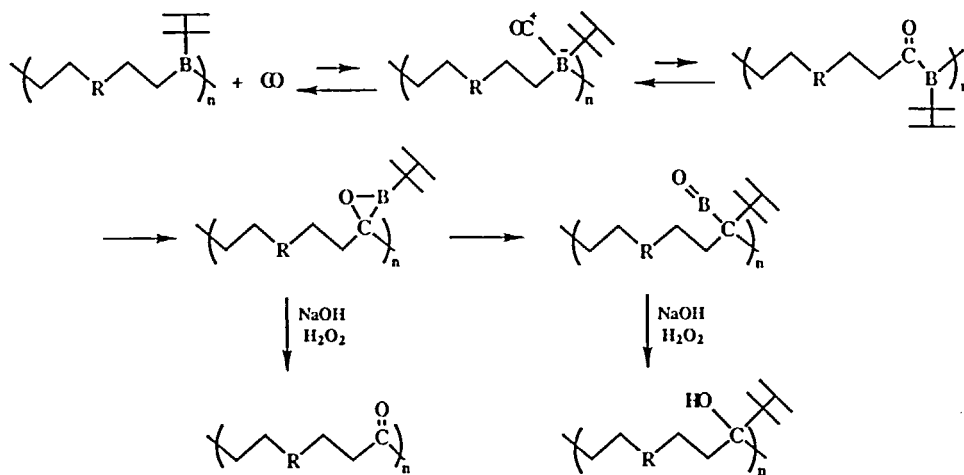
^aPolymerizations were carried out by adding a small excess of thexylborane to a 1 M THF solution of diene at 0°C.

^bGPC (dry THF), polystyrene standard.




SCHEME 2.

a polyalcohol [6]. This conversion includes migrations of the polymer chain and the ethyl group from the boron atom to carbon as shown in Scheme 3. Table 2 summarizes the results of the preparation of polyalcohols from various organoboron polymers. The temperature effect of this reaction on the composition of the polymers obtained (polyalcohol and polyketone segments) is shown in Table 3. When this



SCHEME 3.

TABLE 2. Synthesis of Poly(Alcohol)s by the Reaction of Organoboron Polymers with Carbon Monoxide^a

Run	R	B polymers, \bar{M}_n^b	Poly(alcohol)s		
			\bar{M}_n^c	\bar{M}_w^c	Yield, ^d %
1	$-(\text{CH}_2)_4-$	19,500	4,080	13,500	82
2	$-(\text{CH}_2)_6-$	20,500	4,200	9,600	60
3		14,600	2,990	7,650	74
4	$-\text{CH}_2-\text{C}_6\text{H}_4-\text{CH}_2-$	9,300	5,400	12,300	77
5	$-\text{CH}_2\text{O}(\text{CH}_2)_2\text{OCH}_2-$	1,520	1,280	2,200	24
6	$-\text{CH}_2\text{O}(\text{CH}_2)_4\text{OCH}_2-$	2,280	1,620	2,800	59
7	$-\text{CH}_2\text{O}((\text{CH}_2)_2\text{O})_3\text{CH}_2-$	3,200	2,200	3,720	47
8	$-\text{CH}_2\text{O}-\text{C}_6\text{H}_4-\text{OCH}_2-$	6,800	1,940	3,700	39
9	$-\text{CH}_2\text{O}-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{OCH}_2-$	11,700	2,320	4,400	89

^aReactions were carried out in the presence of 0.1 mL ethylene glycol under carbon monoxide (20–25 kg/cm²) in an autoclave.

^bGPC (dry THF), PS standard.

^cGPC (THF), PS standard.

^dIsolated yield after reprecipitation into methanol/water (v/v = 2/1).

TABLE 3. Reactions of Organoboron Polymer with Carbon Monoxide

Run	Conditions	Composition ^f		\bar{M}_n^g	Yield, ^h %
		Alcohol	Ketone		
1	50°C, 15 h; 120°C, 5 h ^a	100	0	4,080	82
2	50°C, 15 h ^b	50	50	2,500	80
3	RT, 18 h ^b	32	68	2,500	61
4	0°C, 15 h ^b	34	66	590	67
5	-25°C, 40 h ^c	—	—	No polymer	0
6	50°C, 15 h ^d	35	65	3,900	N.D. ⁱ
7	50°C, 15 h ^e	—	—	Gelation	—

^aRun 1: 50°C, 15 h (CO; 25 kg/cm²), and then 120°C, 5 h (after CO was released).

^bRuns 2–4: CO; 20–25 kg/cm².

^cRun 5: CO; 30–35 kg/cm².

^dH₂O (1 equiv.) was added at the carbonylation stage (CO; 30–35 kg/cm²).

^eIn the absence of ethylene glycol.

^fCalculated from ¹H NMR.

^gGPC (THF), PS standard.

^hIsolated yields after reprecipitation into methanol/water (v/v = 2/1).

ⁱNot determined.

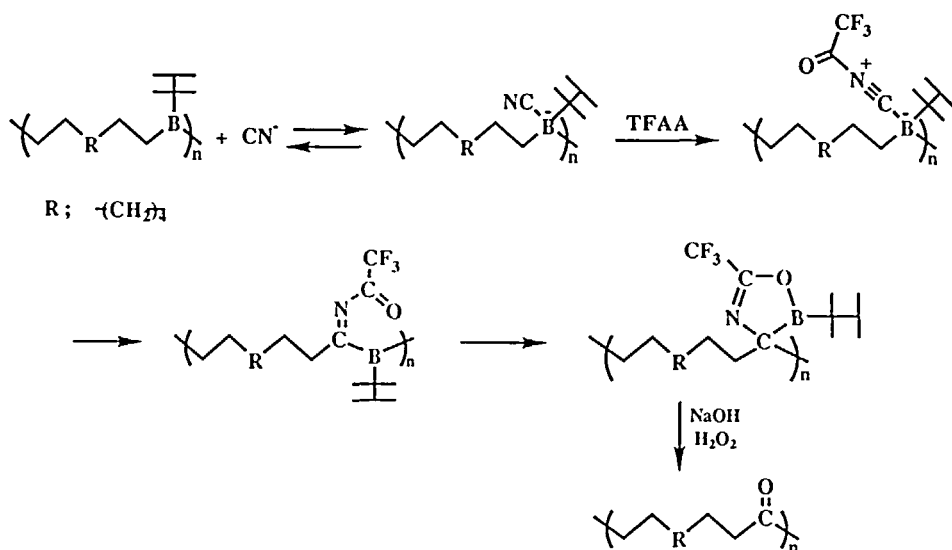
reaction was carried out under milder condition, polyketone segments were included in the polymer structure due to the incomplete migration of the thexyl group. These conversions may offer a new synthetic method for the preparation of poly(alcohol)s from the corresponding dienes.

REACTIONS WITH CYANIDE ANION TO POLYKETONES

For the selective preparation of polyketone, the organoboron polymer prepared by hydroboration polymerization between thexylborane and 1,7-octadiene was subjected to reaction with KCN [7]. After oxidation of the reaction mixture followed by coagulation, the desired polyketone was obtained. The polymer formed was a white solid and stable under air. This stability indicates no C—B bonds in the main chain of the resulting polymer, that is, complete conversion. This reaction also includes the migration of main chains of organoboron polymer from boron to carbon as shown in Scheme 4.

REACTIONS WITH DICHLOROMETHYL METHYL ETHER TO POLYALCOHOLS

As an alternative method for the preparation of polyalcohol from organoboron polymer, dichloromethyl methyl ether (DCME) can be used [8]. Various organoboron polymers prepared by hydroboration polymerization of dienes and thexylborane were reacted with DCME at 0°C in THF followed by treatment with lithium triethylmethoxide. After oxidative treatment with NaOH and H₂O₂, the



SCHEME 4.

corresponding poly(alcohol)s were obtained (Scheme 5, Table 4). The structures of the resulting poly(alcohol)s were the same as those prepared by the reaction with carbon monoxide described above. Because the reaction with carbon monoxide requires relatively severe conditions (e.g., 120°C, 30 kg/cm²) [6], the reaction with DCME provides a more facile way for the conversion of organoboron polymers into poly(alcohol)s under mild conditions.

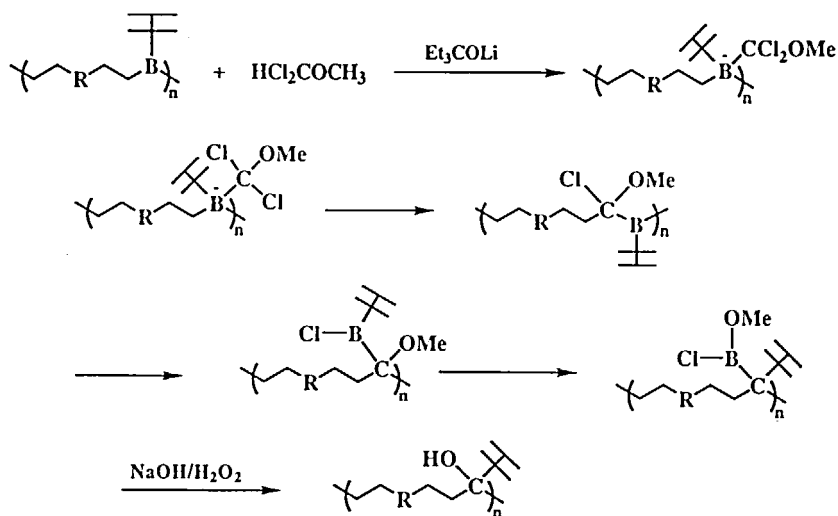
REACTIONS WITH PYRIDINE OR FURAN RING

We also explored novel reactions of organoboron polymers via ring-opening of pyridine or furan moieties. As shown in Scheme 6, the organoboron polymers prepared by hydroboration polymerization were reacted with 2-bromo-6-lithio-pyridine followed by treatment with NaOH to produce the cyano-group-containing polymers [9]. The results are summarized in Table 5.

On the other hand, the reaction of organoboron polymer with α -furyllithium was followed by treatment with acetic acid and then with NaOH and H₂O₂ to form a polymer having primary and tertiary alcohols (Scheme 7) [10]. These conversions include the migration of polymer chains on the boron atom and the ring-opening reactions of pyridine and furan, respectively.






REDUCTIVE TREATMENT OF ORGANOBORON POLYMERS

In the conversions from organoboron polymers prepared by hydroboration polymerization of dienes, reductive treatment instead of oxidative treatment gave different polymers. For example, the organoboron polymer was reacted with DCME followed by treatment with acetic acid. This treatment results in the reduc-



SCHEME 5.

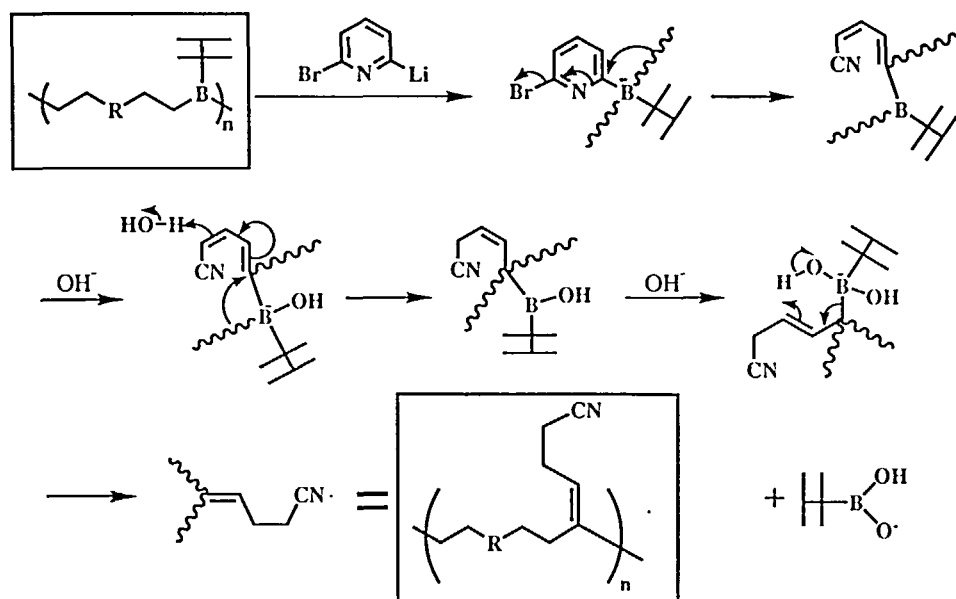
TABLE 4. Synthesis of Poly(Alcohol)s by the Reactions of Organoboron Polymers with DCME^a

Run	R	B polymers, \overline{M}_n^b	Poly(alcohol)s	
			\overline{M}_n^c	\overline{M}_w^c
1	—(CH ₂) ₄ —	12,700	3,600	10,600
2	—(CH ₂) ₆ —	18,400	4,900	14,700
3		19,200	2,200	5,400
4	—CH ₂ —  —CH ₂ —	9,400	1,700	9,700
5	—CH ₂ O(CH ₂) ₂ OCH ₂ —	1,200	780	1,600
6	—CH ₂ O(CH ₂) ₄ OCH ₂ —	1,900	560	1,200
7	—CH ₂ O((CH ₂) ₂ O) ₃ CH ₂ —	1,900	550	1,300
8	—CH ₂ O—  —OCH ₂ —	5,100	1,300	2,400
9	—CH ₂ O—  —  —OCH ₂ —	7,600	2,300	4,700

^aAfter adding 1.2 equiv. DCME to a THF solution of organoboron polymers, 1.5 equiv. of Et₃COLi/*n*-hexane was added at 0°C.


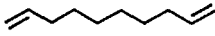
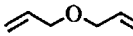




^bGPC (dry THF), PS standard.

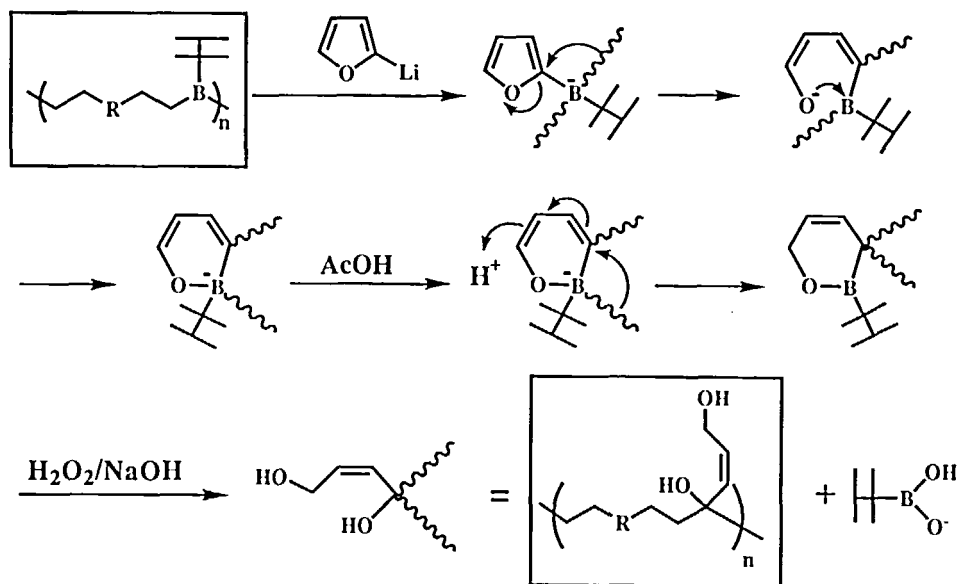
^cGPC (THF), PS standard.



SCHEME 6.

TABLE 5. Reactions of Organoboron Polymers with 2-Bromo-6-lithiopyridine

Run	Diene	\bar{M}_n of B polymer ^{a,b}	\bar{M}_n ^a	\bar{M}_w ^a	Yield, % ^c
1		3,420	3,980	7,500	72
2		3,120	2,990	4,910	57
3		680	1,090	1,950	17 ^d
4		2,670	2,200	2,760	59
5		1,240	1,570	2,120	80
6		1,970	1,490	2,940	71 ^e
7		1,670	1,020	1,400	79 ^e

^aGPC (dry THF), PS standard.^bNot isolated.^cIsolated yields after reprecipitation into diethyl ether/*n*-hexane (v/v = 1/4).^dNot characterized.^eIsolated yields after reprecipitation into MeOH/H₂O (v/v = 1/1).

SCHEME 7.

tive cleavage of carbon—boron bonds. As a result, the hydrocarbon polymer was obtained as shown in Scheme 2 [11]. The reaction of organoboron polymer with α -furyllithium was also followed by reductive treatment to form an allyl-alcohol-branched polymer.

CONCLUSIONS

Generally, the polymers with functional groups described here are not prepared by means of conventional synthetic methods. Thus, these conversions demonstrate the useful and versatile characteristics of organoboron polymers as polymeric precursors to give functional polymers.

A wide variety of dienes can be used as the starting materials in hydroboration polymerization with thexylborane. This means that conversions of organoboron polymers may produce various functional-group-containing polymers. Scheme 2 demonstrates the versatile potential of organoboron polymers prepared by hydroboration polymerization as a novel type of reactive polymers [12].

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