Polymer Bulletin 33, 623–628 (1994)

Polymer Bulletin

Reactions of organoboron polymers prepared by hydroboration polymerization

VI. Reductive treatment after the reaction with α-furyllithium or with dichloromethyl methyl ether[1]

Yoshiki Chujo*, Tomonori Sakurai, and Nobuyuki Takizawa

Division of Polymer Chemistry, Graduate School of Engineering, Kyoto University,
Yoshida, Sakyo-ku, Kyoto 606-01, Japan

Summary

Organoboron polymers consisting of carbon-boron bonds in the main chains were prepared by hydroboration polymerization of various dienes with thexylborane. These polymers were reacted with α-furyllithium followed by treatment with acetic acid to give the corresponding poly(alcohol)s. This conversion includes the migrations of two polymeric main chains from boron atom to carbon and the reductive cleavage of carbon-boron bonds in the resulting boron-containing polymers. The structures of the poly(alcohol)s obtained were characterized by ^{1}H-NMR in comparison with that of model compound, which was prepared by the reaction of dioctylthexylborane with α-furyllithium followed by reductive treatment. The organoboron polymer prepared from 1,7-octadiene and thexylborane was also reacted with dichloromethyl methyl ether followed by acidolysis to form hydrocarbon polymer without obvious scission of polymeric main chain.

Introduction

We have recently explored a novel methodology for the preparation of organoboron polymers consisting of carbon-boron bonds in the main chains. (2-6) We termed this "Hydroboration Polymerization". The organoboron polymers obtained can be regarded as a polymer homologue of trialkylborane and can be used as a novel type of reactive polymers. Thus, versatile reactions of organoboron polymers prepared by hydroboration polymerization have been demonstrated . (7) For example, poly(alcohol)s were obtained by the reactions with carbon monoxide (8) or with dichloromethyl methyl ether (9) followed by oxidative treatment. The reaction with cyanide anion gave poly(ketone)s. (10) The ring-opening reactions of furan (11) or pyridine (12) produced diol- or nitrile-containing polymers, respectively. The polymers having these structures are hardly prepared by means of conventional synthetic methods.

Generally, oxidative treatment of trialkylboranes, e.g., reaction with hydrogen peroxide in the presence of base, is known to cause oxidative cleavage of carbon-boron bonds. (13) Thus, various alcohols or ketones can be prepared from trialkylboranes by this procedure. On the other hand, acidolysis of trialkylboranes is also used in organic synthesis. This treatment means the reductive cleavage of carbon-boron bonds. (13) Here we describe the reductive treatment (acidolysis) of the boron-containing polymers obtained by the reactions of organoboron polymers with α-furyllithium or with dichloromethyl methyl ether.

Results and discussion

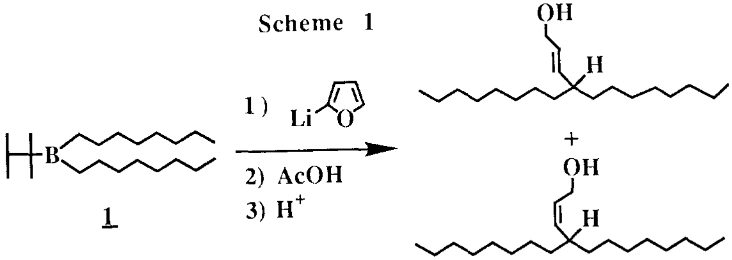
First, a model reaction was carried out using dioctylthexylborane (**1**) according to the reported method. (14) **1** was reacted with α-furyllithium followed by treatment with

---

[1] See references

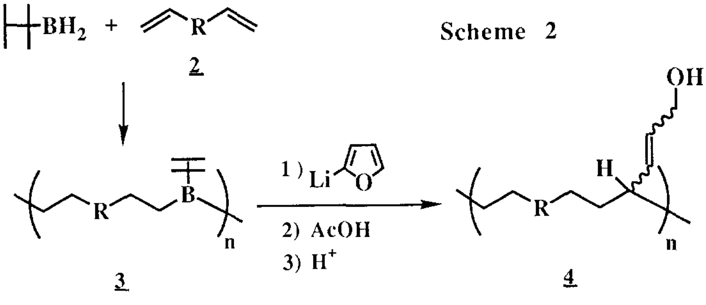
* Corresponding author

acetic acid. After further treatment with aqueous HCl, the reaction mixture was subjected to column chromatography. Trialkylboranes are known to be relatively stable to aqueous HCl, and carboxylic acid is generally used for their reductive treatment. (13) In the present study, however, the addition of HCl might be effective for the reaction with acetic acid, which has already added to the reaction mixture. From the results of IR and ^{1}H-NMR spectra, the main product (71% yield) was proved to be 4-octyl-2-dodecen-1-ol as expected (Scheme 1). This indicates that two primary alkyl (octyl) groups preferentially migrates rather than a tertiary alkyl (thexyl) group. However, two isomers were isolated by column chromatography. Their ^{1}H-NMR spectra are illustrated in Figure 1, from which these two isomers are found to be cis and trans forms. The ratio of cis and trans isomers was almost unity calculated from ^{1}H-NMR. This means no stereospecific regulation around olefin moiety in the product in the present reaction.


Scheme 1

Various organoboron polymers (**3a**-**3c**) were prepared by hydroboration polymerization of the corresponding dienes (**2a**-**2c**) with thexylborane. These organoboron polymers were subjected to GPC measurement and directly used for the following reaction without isolation. In a similar manner described above for a model reaction, these polymers (**3a**-**3c**) were reacted with α-furyllithium followed by treatment with acetic acid and then by the further treatment with aqueous HCl (Scheme 2). These results are summarized in Table 1. In all cases, the corresponding poly(alcohol)s (**4**) were obtained effectively although the molecular weights were a little decreased in comparison with those for the starting organoboron polymers. Instead of the treatment with aqueous HCl (Run 1), the method using additional acetic acid either at room temperature (Run 3) or at 50°C (Run 2) could be used, but lower molecular weight oligomers were obtained. All polymers (**4**) obtained in Runs 1-3 showed the entirely same ^{1}H-NMR and IR spectra.

The structures of the polymers obtained (**4**) were characterized by ^{1}H-NMR spectra. As a typical example, ^{1}H-NMR spectrum of the product (**4a**) prepared from **3a** is illustrated in Figure 1 together with those of model compounds. All peaks for **4a** are very similar to those for the model compounds. However, olefin protons around 5-6 ppm showed a mixture of cis and trans forms in the structure of **4a**. From the integral ratio of these protons, the product poly(alcohol) was found to consist of 1:1 cis-trans mixture.


Scheme 2

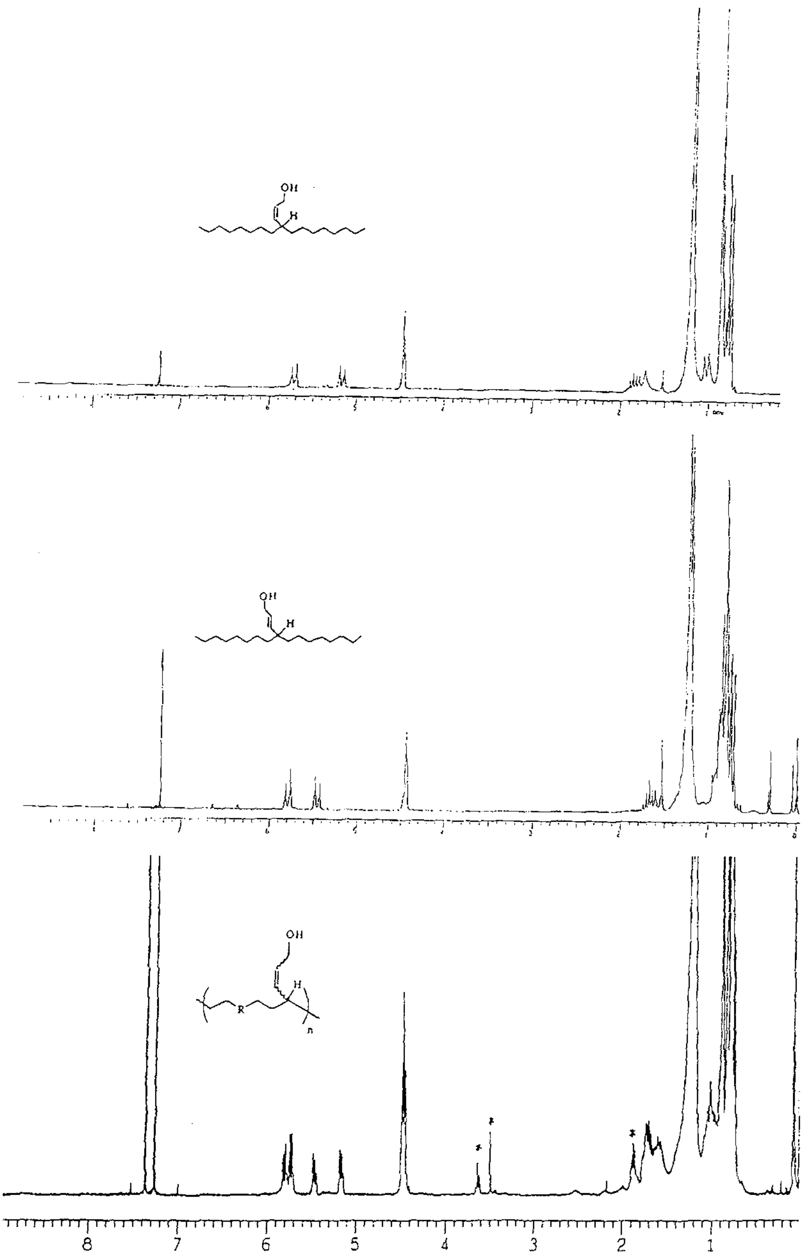
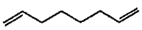
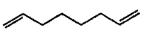
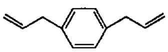
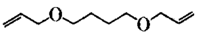


Fig.1. ^{1}H-NMR spectra of 4-octyl-2-dodecen-1-ol (cis- and trans-isomers) and **4a**.

Table 1. Reactions of organoboron polymers with α-furyllithium.

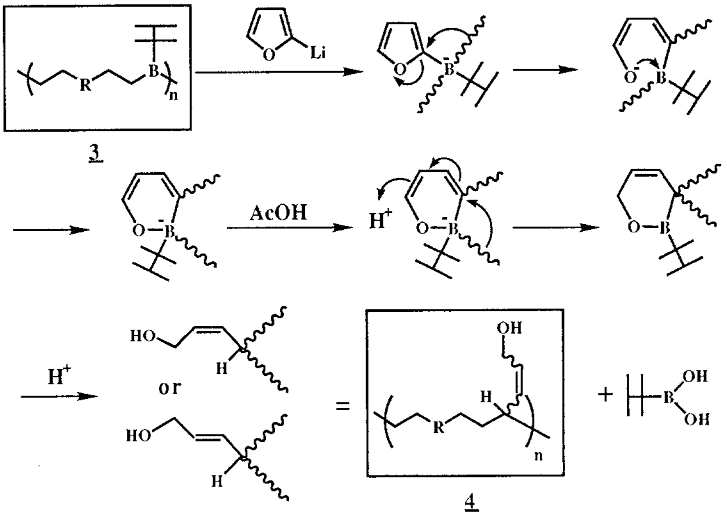
Run	Diene		<u>3</u>	<u>4</u>		
			$\overline{M}_n$ [a) b)]	Yield (%)	$\overline{M}_n$ [a)]	$\overline{M}_w$ [a)]
1[c)]		(<u>2a</u>)	3,100	78	2,700	8,500
2[d)]		(<u>2a</u>)	5,500	91	1,700	11,400
3[e)]		(<u>2a</u>)	5,300	93	1,200	9,500
4[c)]		(<u>2b</u>)	2,400	64	2,900	9,800
5[c)]		(<u>2c</u>)	1,100	—[b)]	460	920

a) GPC (dry THF), polystyrene standards. b) Not isolated. c) Treatment with AcOH and then with HClaq at room temperature. d) Treatment with AcOH at room temperature and then at 50°C. e) Treatment with AcOH at room temperature.

Other protons were also observed in the same region as those for the model componds. The ratio of methyl protons (0.5-1.0 ppm) in **4a**, however, was a little larger than expected. This might be due to thexyl groups at the end of the polymer and/or due to the thexyl protons of the contaminated boric acid derivatives. This phenomenum is similar to the case of the oxidative treatment after the reaction with α-furyllithium reported previously. (11)

The mechanism of the present reaction can be explained as illustrated in Scheme 3. A primary alkyl group is known to be more reactive than a tertiary alkyl group in this intramolecular migration as described in the case of model reaction. Accordingly, it is reasonable to suppose that the migration of the polymer chain is much easier than that of thexyl group. The reaction of **3a** with α-furyllithium gives borate anion, from which one polymer chain migrates from boron to α-carbon of furan ring. This migration causes a

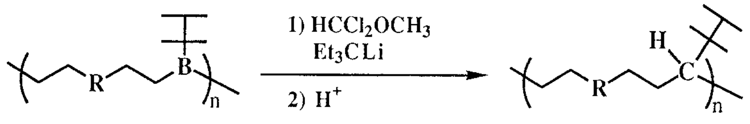
Scheme 3



ring-opening of furan to form six-membered cyclic borate after coordination of oxygen to boron atom. The addition of acetic acid assists the migration of another main chain to give a cyclic boron-containing polymer. The reductive treatment of the resulting polymer produces poly(alcohol) (**4**) after reductive cleavage of O-B-C bond.

The organoboron polymer (**3a**, M_n=2800) prepared by hydroboration polymerization between 1,7-octadiene (**2a**) and thexylborane was reacted with dichloromethyl methyl ether in the presence of lithium 3-ethyl-3-pentanolate, Et_3CLi, in THF at 0°C under nitrogen. This reaction also includes the migration of polymeric main chains from boron atom to carbon. After treatment with acetic acid, the hydrocarbon polymer (**5a**) having the structure shown in Scheme 4 was obtained in 82% yield. The structure of **5a** was supported by ^{1}H-NMR spectrum. The number-average molecular weight of **5a** was found to be 2700. No decrease of the molecular weight was observed in the present reaction in comparison with the molecular weight of the starting **3a**. This means that no scission of carbon-boron bonds takes place during migration reactions.

Scheme 4



3a R=$(CH_2)_4$

5a

In conclusion, the reactions of organoboron polymers prepared by hydroboration polymerization of dienes with thexylborane were successfully followed by acidolysis (reductive treatment) similarly to the oxidative treatment. In other words, the present method may provide more versatility of the organoboron polymers as polymeric precursors for the production of various polymers having a wide variety of functional groups.

Experimental

Materials and instruments

Thexylborane (**1**) was obtained by the reaction between borane-dimethyl sulfide and 2,3-dimethyl-2-butene as reported earlier (15), and was purified by distillation (2). 1,7-Octadiene (**2a**) and divinylbenzene (**2b**) were purified by distillation. Bis(allyl ether) of 1,4-butanediol (**2c**) was prepared according to the reported method. (2) Acetic acid and 1N aqueous HCl was used after nitrogen bubbling. Furan, diethyl ether and tetrahydrofuran were dried over sodium and distilled before use. Dichloromethyl methyl ether was dried over calcium chloride and was distilled. 3-Ethyl-3-pentanol was dried over calcium hydride and purified by distillation. *n*-Butyllithium was used without further purification.

^{1}H-NMR spectra were recorded in $CDCl_3$ on a Hitachi R-600 (60MHz) or on a Varian JEMINI-200 (200MHz) using tetramethylsilane as an internal 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) after calibration with standard polystyrene samples.

Reaction of dioctylthexylborane (1) with α-furyllithium followed by reductive treatment (model reaction)

In a 50-mL round-bottomed flask equipped with a reflux condenser, furan (0.29g, 4.31mmol) and diethyl ether (5mL) were charged under nitrogen. After addition of 2.36mL of 1.6M *n*-butyllithium in *n*-hexane, the reaction mixture was refluxed for 6 hours. On the other hand, dioctylthexylborane (**1**) was prepared by the reaction between thexylborane (0.21g, 2.10mmol) and 1-octene (0.60g, 5.35mmol) in THF at 0°C under nitrogen. A THF solution of **1** was added to a solution of α-furyl-lithium. After stirring overnight at room temperature, acetic acid (0.3mL) was added. After 2 hours, 10mL of 1N aqueous HCl was added. The resulting reaction mixture was extracted with diethyl ether. The product was dried over sodium sulfate and purified by column chromatograpgy (silica gel, *n*-hexane). Total yield of cis- and trans-4-octyl-2-dodecen-1-ol was 71%. ^{1}H-NMR spectra of two isomers of the product are shown in Figure 1.

Synthesis of poly(alcohol)s (4) by the reactions of organoboron polymers (3) with α-furyllithium followed by reductive treatment

A typical procedure is as follows. Organoboron polymer (**3a**) was prepared by the reaction of 1,7-octadiene (**2a**) (0.21g, 1.89mmol) with thexylborane (0.23g, 2.36mmol) in THF at 0°C under nitrogen. The THF solution of **3a** was treated with α-furyllithium similarly as mentioned in the part of model reaction. The product polymer (**4a**) was dissolved in diethyl ether, precipitated into methanol and freeze-dried with benzene. Yield of **4a** was 269mg (78%). ^{1}H-NMR spectrum of **4a** is shown in Figure 1. IR spectrum of **4a** shows the peaks at 3500, 2930 and 1650 cm^{-1}.

4b and **4c** were produced in a similar manner. **4b**: Yield; 64%. ^{1}H-NMR (δ, $CDCl_3$); 1.21-1.94 ($PhCCH_2CH_2$ and CH, m, 8H+1H), 2.38-2.70 ($PhCH_2$, m, 4H), 4.30-4.62 (CH_2O, m, 2H), 5.10-5.96 (CH=CH, m, 2H), 6.81-7.18 (C_6H_4, m, 4H). **4c**: It was difficult to isolate by reprecipitation due to its low molecular weight. ^{1}H-NMR (δ, $CDCl_3$); 1.04-1.25 ($OCCCH_2$, m, 4H), 1.49-1.65 ($OCCH_2$, m, 8H), 1.84-1.90 (CH, m, 1H), 3.04-3.35 (OCH_2CC, m, 8H), 4.27-4.60 (OCH_2, m, 2H), 5.01-5.97 (CH=CH, m, 2H).

Synthesis of hydrocarbon polymer (5) by the reaction of organoboron polymer (3a) with dichloromethyl methyl ether followed by reductive treatment

To a THF solution of organoboron polymer (**3a**) prepared from 1,7-octadiene (**2a**) (0.23g, 2.12mmol) and thexylborane (0.20g, 2.07mmol), dichloromethyl methyl ether (0.24mL, 2.65mmol) and *n*-hexane solution (1.51N, 1.7mL) of lithium 3-ethyl-3-pentanolate were added at 0°C under nitrogen. After the reaction at room temperature for 24 hours, 0.7mL of acetic acid was added. The product polymer (**5a**) was extracted with THF, precipitated into ethanol/water (v/v=1/1) and freeze-dried with benzene. **5a** was isolated in 82% yield. **5a**: ^{1}H-NMR (δ, $CDCl_3$); 0.62-0.98 (CH_3, m, 12H), 1.06-1.92 (CH_2 and CH, m, 16H+1H+1H).

References

1. For parts I-V, see references 8, 10, 9, 11 and 12, respectively.
2. Chujo Y, Tomita I, Hashiguchi Y, Tanigawa H, Ihara E, Saegusa T (1991) Macromolecules 24: 345
3. Chujo Y, Tomita I, Hashiguchi Y, Saegusa T (1992) Macromolecules 25: 33
4. Chujo Y, Tomita I, Saegusa T (1992) Polym Bull 27: 375
5. Chujo Y, Tomita I, Saegusa T (1993) Makromol Chem Macromol Symp 70/71: 47
6. Chujo Y, Takizawa N, Sakurai T (1994) J Chem Soc Chem Commun 227
7. Chujo Y (1994) J Macromol Sci Pure and Appl Chem A31: 1647
8. Chujo Y, Tomita I, Hashiguchi Y, Saegusa T (1991) Macromolecules 24: 3010
9. Chujo Y, Tomita I, Saegusa T (1991) Polym Bull 26: 165
10. Chujo Y, Tomita I, Hashiguchi Y, Saegusa T (1991) Polym Bull 25: 1
11. Chujo Y, Morimoto M, Tomita I (1992) Polym Bull 29: 617
12. Chujo Y, Morimoto M, Tomita I (1993) *Polym. J.* 25: 891
13. Pelter A, Smith K, Brown HC (1988) Borane Reagents, Academic Press, London
14. Suzuki A, Miyaura N, Itoh M (1971) Tetrahedron 27:2775
15. Brown HC, Mandal AK, Kulkarni SU (1977) J Org Chem 42: 1392

Received: 29 August 1994/Accepted: 19 September 1994