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Reactions of organoboron polymers prepared by hydroboration polymerization

IV. Synthesis of polyalcohols having primary and tertiary hydroxyl groups by the reaction with α-furyllithium[1]

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Summary

Organoboron polymers were prepared by hydroboration polymerization between various dienes and thexylborane. These polymers were reacted with α-furyllithium followed by the treatment with acetic acid and then by the oxidative treatment to give the corresponding polyalcohols having primary and tertiary hydroxyl groups. The structures of the polyalcohols obtained were characterized by ^{1}H-NMR compared with that for model compound, which was prepared by the reaction of dioctylthexylborane with α-furyllithium. These conversions from organoboron polymers to polyalcohols include the migrations of two polymeric chains from boron atom to carbon and the ring-opening of furan ring.

Introduction

Organoboron polymers are versatile reactive polymers for the preparation of a wide variety of functional polymers. We have recently explored "Hydroboration Polymerization" as a novel methodology for the preparation of organoboron polymers consisting of carbon-boron bonds in the main chains. [3] These organoboron polymers were used as precursor polymers for the preparation of polyalcohols or polyketones by the reactions with carbon monoxide [4], cyanide anion [5], or α,α-dichloromethyl methyl ether [6], respectively. These conversions are demonstrated in Scheme 1.

Generally, organoboron compounds are very useful reagents or intermediates for the preparation of various functional compounds. [7] For example, trialkylboranes gave 4,4-dialkyl-*cis*-2-butene-1,4-diols by the reaction with α-furyllithium followed by the oxidative treatment with alkaline hydrogen peroxide (Scheme 2). [8] The present paper describes the reactions of organoboron polymers with α-furyllithium followed by the treatment with acetic acid and then by the oxidative treatment to give the corresponding polyalcohols having primary and tertiary hydroxyl groups.

Footnotes 1 and 2 see references

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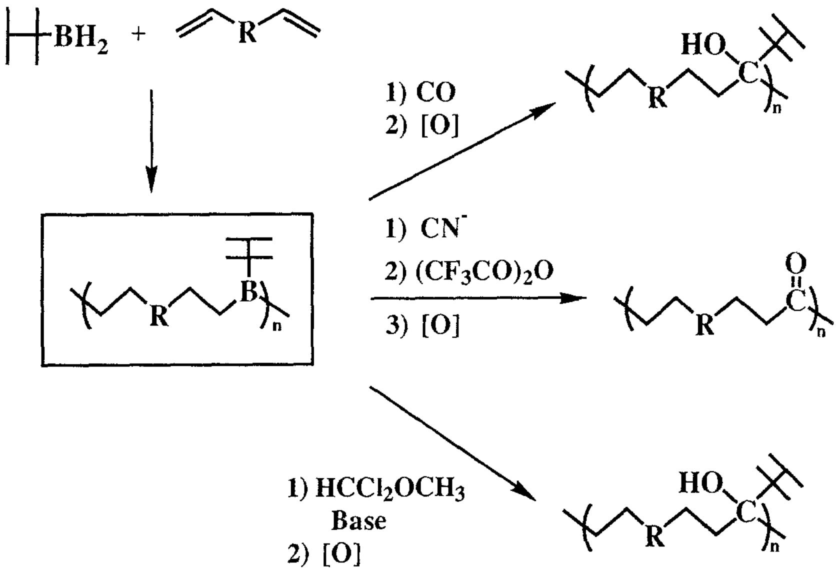
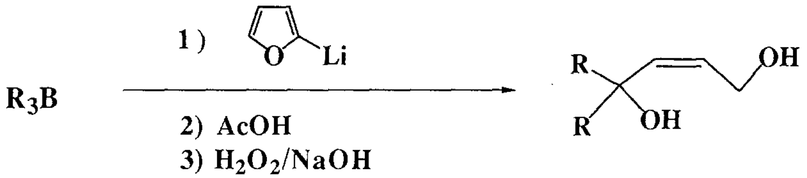
Scheme 1



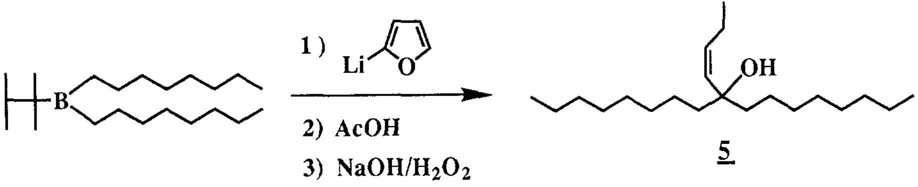
Scheme 2



Results and Discussion

A model reaction was carried out using dioctylthexylborane according to the reported method (Scheme 3) [8]. The structure of the product (4-octyl-*cis*-2-dodecene-1,4-diol, **5**) was confirmed by ^{1}H-NMR. The ^{1}H-NMR spectrum is shown in Figure 1(a), in which 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 of **5**. This result indicates that the present reaction includes exclusively the migration of two primary alkyl (octyl) groups rather than a tertiary alkyl (thexyl) group.

Scheme 3



5

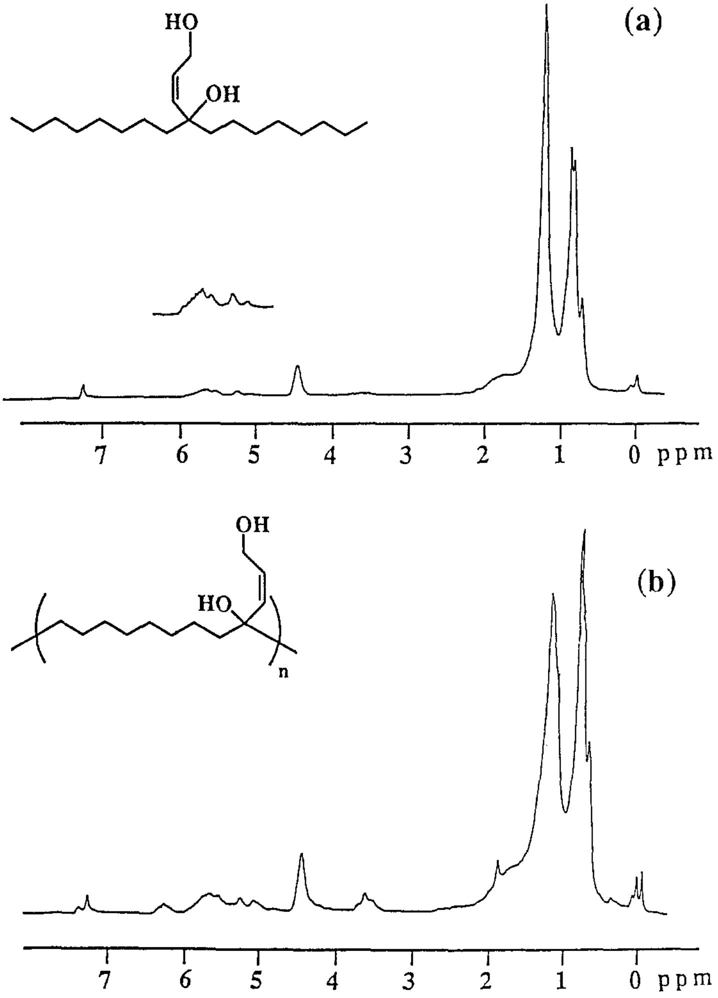
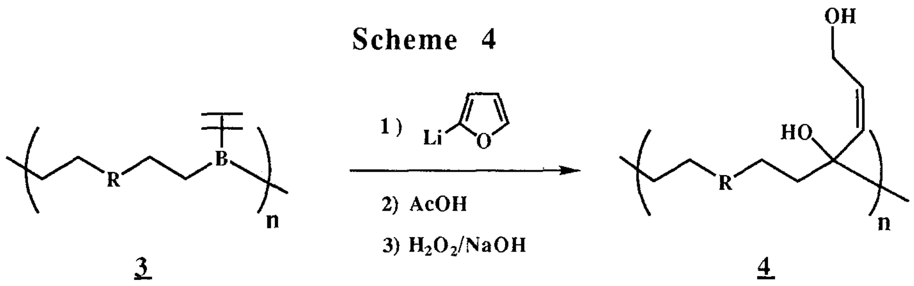


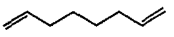
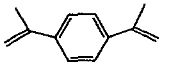
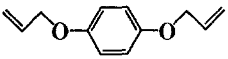
Figure 1. ^{1}H-NMR spectra of (a) model compound (5) and (b) diol-containing polymer (4a).

Scheme 4



Similarly, as shown in Scheme 4, the reactions of organoboron polymers (**3**) with α-furyllithium followed by the addition of acetic acid and the oxidative treatment were carried out to produce the polyalcohols having primary and tertiary hydroxyl groups (**4**). The starting organoboron polymers (**3a**-**3c**) were easily prepared by the reactions of various dienes (**2a**-**2c**) with thexylborane (**1**), respectively. **3a**-**3c** were used without isolation for the following reactions with α-furyllithium. The molecular weights of **3** and **4** were determined by GPC using THF as an eluent. The results are summarized in Table I, in which the number-average molecular weights of **4** were close to those of **3**. This means that no obvious scission of carbon-boron bonds of organoboron polymers (**3**) took place during the present reactions.

Table I. Reactions of Organoboron Polymers with α-Furyllithium

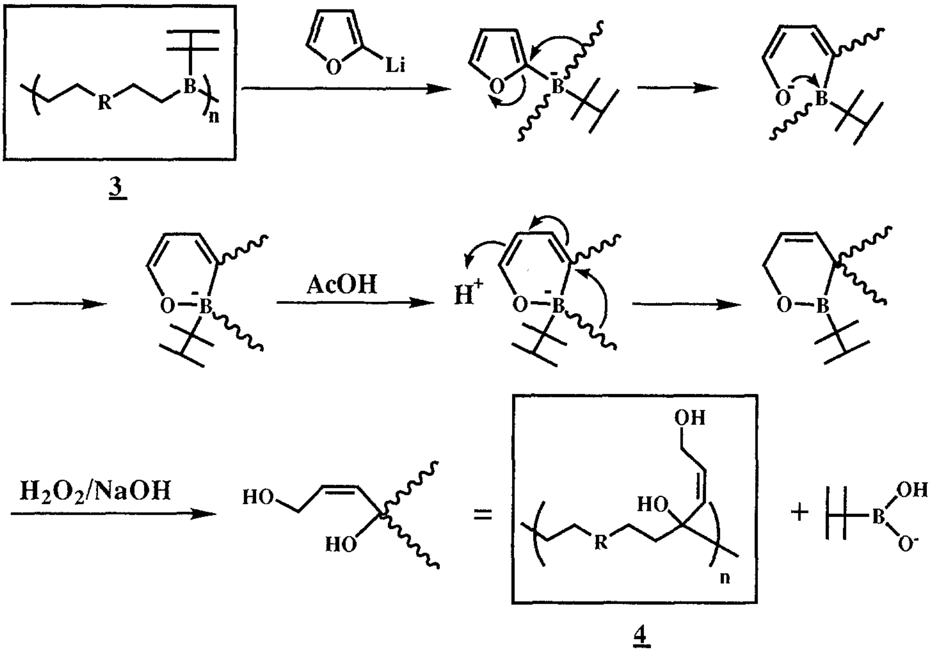
Run	Diene	3^a)	4	
		$\overline{M}n^{b)}$	$\overline{M}n^{b)}$	$\overline{M}w^{b)}$
1	 (2a)	3,970	2,890	6,750
2	 (2b)	1,280	1,330	2,620
3	 (2c)	1,190	1,200	2,020

a) Not isolated. b) GPC (dry THF, polystyrene standard).

The structures of the polymers obtained were characterized by ^{1}H-NMR. As a typical example, ^{1}H-NMR spectrum of **4a** is shown in Figure 1(b). The olefinic protons and methylene protons adjacent to hydroxyl groups were observed in the same region as the model compound (**5**). However, the ratio of methyl protons (0.5-1.0 ppm) in **4a** was larger than that of **5**. This might be due to the end thexyl groups of the polymer and also due to the thexyl protons of the contained boric acid derivatives. In fact, this peak was decreased by the repeated reprecipitations of the polymer into *n*-hexane. This purification method, however, caused very low yields of the product because the polymer obtained was partly soluble in *n*-hexane. These results indicate that the polymer obtained was contaminated with boric acid derivatives having thexyl groups probably due to the coordinations of hydroxyl groups to boron atoms. Similarly, the polyalcohols obtained from **3b** and **3c** could not be isolated in their pure states. However, it should be noted here that the resulting polymers were found to include no unreacted carbon-boron bonds remained from the results of air-bubbling experiments. No decrease of the molecular weights of the polymers obtained was observed under the oxidative condition, which caused the scission of carbon-boron bonds.

Referred to the proposed mechanism for the reaction of trialkylborane with α-furyllithium [8], the present polymer reaction can be considered to proceed as shown in Scheme 5. As mentioned before, a primary alkyl group is known to be more reactive than a tertiary alkyl group in this intramolecular migration. Accordingly, in the present reaction, 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. In this mechanism, the reaction of **3** with α-furyllithium affords lithium 2-furyltrialkylborate, from which one polymer chain migrates from boron atom to α-carbon of furan ring, followed by its ring-opening. Then, the coordination of oxygen atom to boron atom gave the six-membered cyclic borate. [9] After the migration of another polymer chain in the addition of acetic acid, the corresponding polyalcohol was produced with the ring-opening of the cyclic borate by the treatment with hydrogen peroxide/sodium hydroxide. The large different reactivity between primary and tertiary alkyl groups should make it possible to form the polymer structure from organoboron polymer without obvious scission of the main chain.

Scheme 5



Experimental Section

Materials and Instruments. Thexylborane (**1**) was prepared by the reaction of borane-dimethylsulfide complex with 2,3-dimethyl-2-butene [10] and was purified by distillation. 1-Octene, **2a** and **2b** were purified by distillation. **2c** was prepared from hydroquinone and allyl bromide, and was purified by recrystallization. Acetic acid was purified by adding 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 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 analysis was 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 (Model Reaction). A 30-mL round-bottomed flask equipped with a reflux condenser and a bar of magnetic stirrer was flushed with nitrogen. The flask was charged with 0.27mL (3.71 mmol) 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 6 hours. Then, a THF solution of dioctylthexylborane, which was prepared from 0.2mL of thexylborane (1.55 mmol) and 0.8mL of 1-octene in THF at 0°C and was isolated by vacuum drying, was added by a syringe to the solution of α-furyllithium at room temperature. After the 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 5 hours. 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, $CDCl_3$); 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 Polyalcohols (4) by the Reactions of Organoboron Polymers (3) with α-Furyllithium. A typical procedure is as follows: **3a** was prepared by the reaction of **2a** (0.141g, 1.28 mmol) with thexylborane (0.167mL, 1.28 mmol) in THF at 0°C. The THF solution of **3a** was treated similarly 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. **4b** and **4c** were produced in a similar manner.

References and Notes

1. For parts I, II, and III, see references 4, 5, and 6, respectively.
2. Present address: Research Laboratory of Resouces Utilization, Tokyo Institute of Technology, Nagatsuda, Midori-ku, Yokohama 227, Japan
3. a) Y. Chujo, I. Tomita, Y. Hashiguchi, H. Tanigawa, E. Ihara, and T. Saegusa, *Macromolecules*, **24**, 345 (1991). b) Y. Chujo, I. Tomita, Y. Hashiguchi, and T. Saegusa, *Macromolecules*, **25**, 33 (1992). c) Y. Chujo, I. Tomita, and T. Saegusa, *Polym. Bull.*, **27**, 375 (1992).
4. Y. Chujo, I. Tomita, Y. Hashiguchi, and T. Saegusa, *Macromolecules*, **24**, 3010 (1991).
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6. Y. Chujo, I. Tomita, and T. Saegusa, *Polym. Bull.*, **26**, 165 (1991).
7. a) A. Pelter, K. Smith, and H. C. Brown, *Borane Reagents*, Academic Press, London (1988). b) H. C. Brown, *Organic Synthesis via Boranes*, Wiley-Interscience, New York (1975).
8. A. Suzuki, N. Miyaura, and M. Itoh, *Tetrahedron*, **27**, 2775 (1971).

9. The cyclic borate was isolated by column chromatography in reference 8, from which the proposed mechanism was supposed.
10. H. C. Brown, A. K. Mandal, and S. U. Kulkarni, *J. Org. Chem.*, **42**, 1392 (1977).

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