Polymer Bulletin 38, 531–536 (1997)

Polymer Bulletin

Synthesis of novel organoboron polymers by hydroboration polymerization of bisallene compounds

Noriyoshi Matsumi, Yoshiki Chujo*

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

Received: 20 December 1996/Accepted: 7 February 1997

Summary

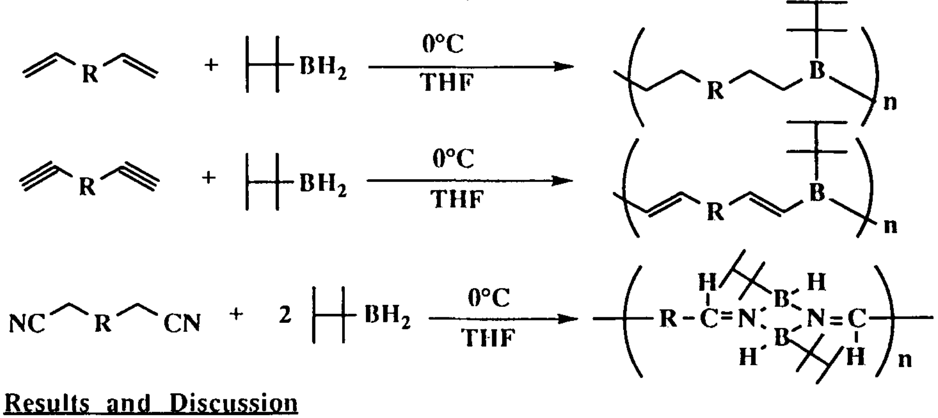
This paper describes synthesis of novel organoboron polymers by hydroboration polymerization of bisallene compounds. The polymers were prepared by polyaddition between thexylborane and bisallenes. The polymers obtained have allylborane units in their main chains and can be expected as a novel type of reactive polymers. The polymer was subjected to a chain transformation reaction and the corresponding polyalcohol was obtained. Hydroboration polymerization of bisallene with mesitylborane was also carried out. It was found that the polymer prepared from mesitylborane showed higher stability than that prepared from thexylborane.

Introduction

Recently, we reported synthesis of organoboron polymers by hydroboration polymerization of dienes [1], diynes [2] and dicyano compounds [3] with thexylborane (Scheme I). The polymers have boron atoms in their main chains and were used as a novel type of reactive polymers [4]. For example, the polymers prepared from dienes were reacted with carbon monoxide [5] or with potassium cyanide [6] followed by the oxidative treatment to give poly(alcohol)s or poly(ketone)s, respectively.

Here, we wish to report synthesis of novel organoboron polymers by hydroboration polymerization of bisallene compounds that are known to have high reactivity toward hydroboration reaction.

Scheme I



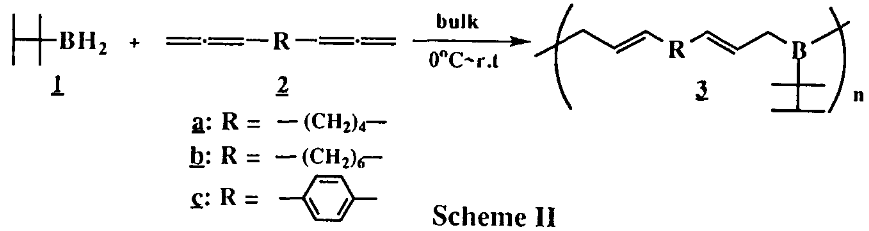
Results and Discussion

As a typical example, the hydroboration polymerization between 1,2,10,11-dodecatetraene (2b) and thexylborane (1) was carried out in bulk (Scheme II). 2b was added to 1 at 0°C and then the reaction mixture was gradually warmed up to room temperature. After reprecipitation into DMF, a colorless gum was obtained. The polymer (3b) obtained was soluble in common organic solvents such as THF, benzene,

---

* Corresponding author

and chloroform. The number-average molecular weight of this polymer was estimated to be 6400 from the result of GPC based on polystyrene calibration curves.



Scheme II

The structure of the polymer was supported by ^{1}H- and ^{11}B-NMR spectra, and also by oxidative decomposition. ^{11}B-NMR spectrum of 3b is represented in Figure 1, in which the main peak corresponding to diallylalkylborane is observed at 54.1 ppm. The molecular weight of the polymer increased when the feed ratio of two monomers approached to unity. This result indicates that the present polymerization proceeds in a polyaddition manner. The results of polymerization by using various bisallene compounds 2a-2c are shown in Table I.

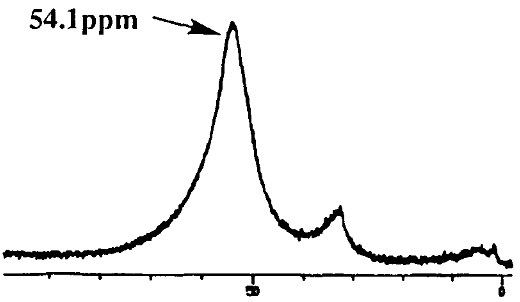
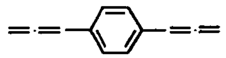


Figure 1. ^{11}B-NMR spectrum of polymer 3b.

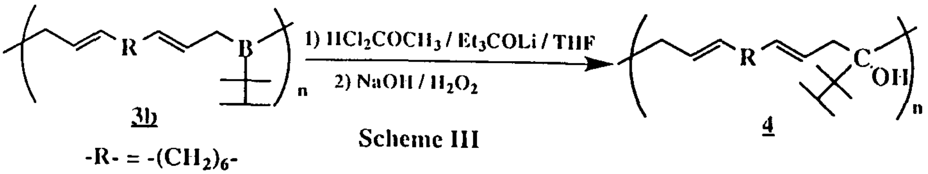
Table I. Hydroboration Polymerization of Various Bisallenes [a)]

run	bisallenes (2)		1/2	Mw [b)]	Mn [b)]	yield (%) [c)]
1	$=\cdot=-(CH_2)_4-=\cdot=$	(2a)	1.12	1800	1200	31
2	$=\cdot=-(CH_2)_6-=\cdot=$	(2b)	1.25	10700	6400	36
3		(2c)	1.17	1200	1100	21

a) Reactions were carried out in bulk at 0°C, and then warmed up to r.t.
b) GPC (THF), polystyrene standards. c) Isolated yields after reprecipitation into DMF.

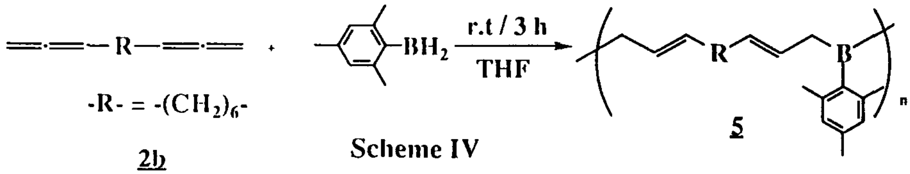
As a bisallene monomer, 1,2,8,9-decatetraene (2a) and 1,4-diallenylbenzene (2c) also gave the corresponding polymers. However, the molecular weights of these polymers were relatively lower than that prepared from 2b. This is probably bacause some isomerizations of bisallenes took place during the course of polymerization due to lower stability of these monomers in comparison with 2b.

The polymer prepared from 2b was subjected to a chain transformation reaction (DCME rearrangement [7]). Dichloromethyl methyl ether (DCME) and lithium alkoxide of 3-ethyl-3-pentanol in n-hexane was added to a THF solution of the polymer (3b) at 0°C. The reaction mixture was stirried at room temperature for 24h followed by oxidative treatment with H_2O_2/NaOH to give the corresponding polyalcohol (Mn 1000, yield 61%) (Scheme III).



Scheme III

In hydroboration polymerization of 2b, mesitylborane was also used as a borane monomer. Mesitylborane is known to have high stability toward air and to moisture [8] so that the corresponding polymer is expected to have such properties.



Scheme IV

As shown in Scheme IV, the polymerization was carried out by adding 2b to 1.0 M THF solution of mesitylborane at room temperature and the resulting mixture was stirred for 3h. After reprecipitation into MeOH, a white gum was obtained (43% yield). This polymeric product was soluble in common organic solvents such as THF, benzene, chloroform. The number-average molecular weight of the polymer was estimated to be 3300 by GPC based on polystyrene calibration curves.

To examine air stability of the polymer obtained (5), air-bubbling was peformed in THF solutions of polymer 3b and 5 respectively. The decomposition of polymer was followed by GPC measurement. As shown in Figure 2, the polymer prepared from thexylborane was easily decomposed by 1h air-bubbling. In contrast, the polymer prepared from mesitylborane was, though still gradually decomposed, found to have much higher stability against air.

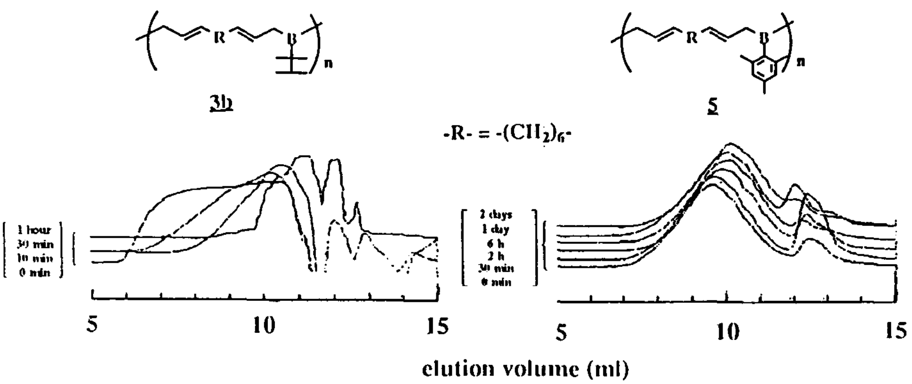


Figure 2. GPC traces of the products before and after air-bubbling in THF solution of organoboron polymers.

Thermal stability of these polymers was also investigated by TGA measurement and the results are shown in Figure 3. The weight loss curve of polymer 5 is shifted to higher temperature region than that of polymer 3b, which shows that the polymer prepared from mesitylborane has higher thermal stability compared with that prepared from thexylborane. This higher stability of the polymer 5 than 3b might be explained as follows. One is sterical hindrance in 5 around boron atom with bulky mesityl group substituent which prevents attack of oxygen or moisture to boron atom. The other is the effect of π-electron donated from benzene ring of mesityl group to vacant p-orbital of boron atom.

In conclusion, novel organoboron polymers having allylborane units in their main chains were prepared by hydroboration polymerization of bisallenes with thexylborane. The obtained polymer was relatively unstable against air, but it was converted to polyalcohol by chain transfomation reaction. Hydroboration polymerization of bisallene with mesitylborane also gave the corresponding organoboron polymer. This polymer was found to have high stability against air and thermal treatment, and is expected as more stable type of reactive polymers.

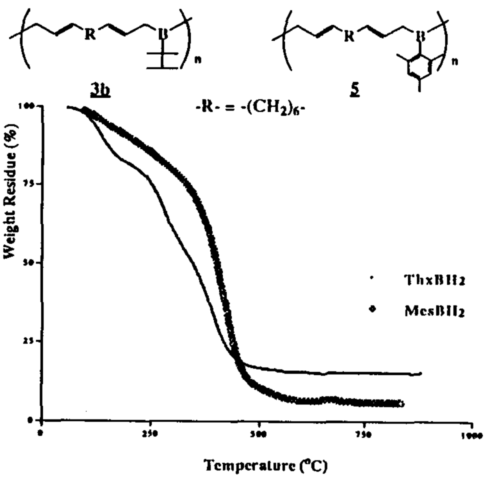


Figure 3. TGA (10^{o}C/min.) traces of organoboron polymers under nitrogen.

Experimental Section

Materials and Instruments. Tetrahydrofuran, 1,7-octadiene, 1,9-decadiene, and n-pentane were dried over sodium and distilled before use. DMF and trimethoxyborane were dried over calcium hydride and distilled. Methanol was dried over magnesium and distilled. Commercially available dichloromethyl methyl ether (DCME), 2-bromomesitylene, and p-divinylbenzene were distilled before use. Potassium t-butoxide, tribromomethane, sodium hydroxide, and hydrogen peroxide (30%) were used without further purification. Lithium alkoxide of 3-ethyl-3-pentanol was prepared by adding an equimolar amount of n-butyllithium/n-hexane to 3-ethyl-3-pentanol at 0^{o}C. Methyllithium and n-butyllithium in n-hexane were purchased from Aldrich.

^{1}H-NMR spectrum and ^{11}B-NMR spectrum were recorded in $CDCl_3$ on a JEOL EX-270 instrument. Gel permeation chromatographic analysis was carried out on a Tosoh G3000H$_{Xl}$ by using THF as an eluent after calibration with standard polystyrene samples. IR spectrum was obtained on a Perkin Elmer 1600 spectrometer. Thermogravimetric analysis (TGA) was made on a Shimadzu DT-30 instrument (10^{o}C/min).

Synthesis of Bisallenes Bisallenes were prepared according to the previously reported method for allenes [9]. Carben addition reaction (Simons-Smith reaction) of diene compounds followed by the treatment with methyllithium gave the corresponding bisallene compounds. A typical procedure for bisallene **2b** is as follows. To a n-pentane (100 ml) solution of 1,9-decadiene (30.0 g, 0.217 mol) suspended with potassium t-butoxide (56.5 g, 0.504 mol), tribromomethane (115.3 g, 0.456 mmol) was added dropwise at -15^{o}C over a period of 6-7 h. When the addition was completed, the reaction mixture was allowed to warm to room temperature and left stirring overnight. Water was added to the reaction mixture followed by the addition of 10% aqueous hydrochloric acid to neutralize the slightly basic solution. The organic layer was separated, and the aqueous layer was extracted with two portions of n-pentane, and the combined n-pentane solutions were washed with three 50 ml portions of water. The n-pentane solution was dried over anhydrous magnesium sulfate and filtered, and then n-pentane was evaporated. Removing residue at 150^{o}C, 1.0 mmHg gave the crude product as a brown solid. The crude carben adduct was suspended in 100 ml ether and methyllithium in ether (1.46M, 200 ml, 0.292 mol) was added at -30^{o}C to -40^{o}C during 1h. After the addition was completed, the reagent was decomposed by dropwise addition of 50 ml of water. An additional 200 ml of water was then added, and the ether layer was separated. The aqueous layer was extracted with three 30 ml portions of ether. The combined ether solutions were washed with 30 ml portions of water until neutral and were dried over magnesium sulfate. The latter was filtered and the evaporation of ether gave a yellow oil. The crude product was purified by column chlomatography (n-pentane) and then dried *in vacuo*. Bisallene **2b** was obtained as a colorless oil (2.30 g) in 7% yield. Bisallenes **2a** and **2c** were also obtained by the same procedure, by using 1,7-octadiene and p-divinylbenzene respectively instead of 1,9-decadiene. ^1H-NMR (270 MHz) (δ, ppm) bisallene **2a** 1.42 ($-CH_2-$, m, 4H), 2.02 ($-C\mathit{H}_2-CH=C$, m, 4H), 4.67 ($-CH=C=C\mathit{H}_2$, s, 4H), 5.07 ($-C\mathit{H}=C=CH_2$, t, J_{C-H} = 92.6 Hz, 2H); bisallene **2b** 1.34 ($-CH_2^-$, m, 8H), 1.98 ($-C\mathit{H}_2-CH=C$, m, 4H), 4.64 ($-CH=C=C\mathit{H}_2$, s, 4H), 5.07 ($-C\mathit{H}=C=CH_2$, t, J_{C-H} = 92.4 Hz, 2H); bisallene **2c** 5.06 ($-CH=C=C\mathit{H}_2$, s, 4H), 6.17 ($-C\mathit{H}=C=CH_2$, s, 2H), 7.28 (benzene ring, m, 4H).

Hydroboration Polymerization of Bisallene 2b with Thexylborane. A typical procedure is as follows. To thexylborane (0.098 g, 1.0 mmol), bisallene **2b** (0.145 g, 0.89 mmol) was added at 0°C under nitrogen. The reaction mixture was allowed to warm to room temperature, and stirred for 4h at room temperature. The evaporation of solvent gave a colorless gum in a quantitative yield. **3b** was further purified by reprecipitation from THF solution into DMF. Isolated yield was 41%. ^1H-NMR (270 MHz) (δ, ppm) 0.73 ($\mathit{Me}_2C\mathit{Me}_2C$, 12H), 1.20 ($-CH_2-$, 12H), 1.75 ($CH_2-B$, 4H), 4.94 ($C\mathit{H}=CH-CH_2-B$, 2H), 5.29 ($CH=C\mathit{H}-CH_2-B$, 2H) ;$^{11}B$-NMR (270 MHz) ($\delta$, ppm) 54.1.

Synthesis of Mesitylborane. Mesitylborane was prepared according to the reported method [7]. The modified procedure is as follows.

Dimethoxymesitylborane To magnesium turnings (3.107 g, 127.8g-atm) and a crystal iodine, a solution of 2-bromomesitylene (23.40 g, 117.5 mmol) in THF (80 ml) was added dropwise at room temperature. The reaction mixture was refluxed for 3h and cooled to room temperature. The THF solution of prepared Grignard reagent was added dropwise to an ether (80 ml) solution of trimethoxyborane (26 ml, 229 mmol) at -15°C under nitrogen. After stirring for 3h at -15°C, the mixture was allowed to warm to room temperature and left stirring overnight. Then the reaction mixture was filtered under nitrogen and the precipitated salts were then washed with dry n-pentane (20 ml). The combined filtrates were concentrated (70°C, 760 mmHg) and distilled to give dimethoxymesitylborane (11.60 g, 51%, 76°C/ 5.0 mmHg). ^1H-NMR (270 MHz) (δ , ppm) 2.27($-CH_3$, s, 6H), 2.29 ($-CH_3$, s, 3H), 3.59 ($-OCH_3$, s, 6H), 6.84 (C_6H_2, s, 2H); ^{11}B-NMR (270MHz) δ 31.7.

Mesitylborane To a solution of dimethoxymesitylborane (1.988 g, 10.13 mmol) in ether (40 ml) and pentane (10 ml) was added a solution of lithium aluminium hydride (0.410 g, 10.35 mmol) in ether (20 ml) at 0°C under nitrogen. The mixture was allowed to warm to room temperature and stirred for 3h. The reaction mixture was filtered under nitrogen and the precipitated salts were then washed with ether (20 ml) and pentane (5 ml). To the combined filtrates was added trimethylsilyl chloride (1.20 ml, 10.1 mmol) dropwise and the mixture was stirred at room temperature for 3h. The precipitate was removed by decantation. The solvent was removed under reduced pressure to give mesitylborane as a white crystal (0.929g, 70%, mp 46°C). ^1H-NMR (270 MHz) (δ, ppm) 2.32 ($-CH_3$, s, 3H), 2.39 ($-CH_3$, s, 6H), 6.92 (C_6H_2, s, 2H).; ^{11}B-NMR (270 MHz) δ 22.4.

Hydroboration Polymerization of Bisallene 2b with Mesitylborane. A typical procedure is as follows. To a 1.0M THF solution of mesitylborane (0.168 g, 1.28 mmol), 2b (0.179 g, 1.10 mmol) was added at room temperature under nitrogen. The reaction mixuture was stirred for 3h. The evaporation of solvent gave a white gum in a quantitative yield. 5 was further purified by reprecipitation from THF solution into MeOH. Isolated yield was 43%. ^{1}H-NMR (270 MHz) (δ, ppm) 1.29 (-CH_2-, 12H), 1.55 ($\mathrm{C}H_2$-B, 4H) 2.16 (Me, 3H), 2.31 (Me, 6H), 4.66 ($\mathrm{C}H$=CH-CH_2-B, 2H), 5.05 (CH=$\mathrm{C}H$-CH_2-B, 2H) ;^{11}B-NMR (270 MHz) (δ, ppm) 30.5.

DCME Rearrangement of Organoboron Polymer 3b. To a THF solution of polymer 3b prepared from 2b (0.286 g, 1.77 mmol) and thexylborane (0.187 g, 1.91 mmol), dichloromethyl methyl ether (DCME) (0.236 g, 2.05 mmol) and lithium alkoxide of 3-ethyl-3-pentanol in n-hexane (1.64 N, 1.8 ml) was added at 0°C under nitrogen and stirred for 24h at room temperature. After the treatment with aqueous sodium hydroxide (6N, 6 ml) and hydrogen peroxide (30%, 6 ml) at 50°C for 3h, the reaction mixture was extracted with three 50 ml portions of THF and dried over sodium sulfate. After evaporation with methanol/benzene (ten times) under normal pressure, freeze-drying with benzene gave 4 in a quantitative yield. This crude product was washed with ethanol/water (v/v=1/1). 4 was isolated as a colorless oil (0.296 g) in 61% yield. IR (ν, cm^{-1}) 3416 (-OH), 1598 (C=C); ^{1}H-NMR (270 MHz) (δ, ppm) 0.72 (Me_2CMe_2C, 12H), 1.17 (-CH_2-, 16H), 3.34 (OH, 1H), 4.91 ($\mathrm{C}H$=CH-CH_2-C-Thexyl, 2H), 5.44 (CH=$\mathrm{C}H$-CH_2-C-Thexyl, 2H).

Air Stability of Organoboron Polymers. The air stability of organoboron polymers toward air oxidation was examined by monitoring the change of the molecular weights by GPC curve during an oxidation experiment, in which a stream of air was bubbled into a THF solution of organoboron polymers. After the designated time, the resulting polymer was characterized by GPC measurement.

References and Notes

1. (a) Chujo Y, Tomita I, Hashiguchi Y, Tanigawa H, Ihara E, Saegusa T (1991) Macromolecules 24:345 (b) Chujo Y, Tomita I, Saegusa T (1992) Polym Bull 27:375
2. Chujo Y, Tomita I, Hashiguchi Y, Saegusa T (1992) Macromolecules 25:33
3. (a) Chujo Y, Tomita I, Murata N, Mauermmann H, Saegusa T (1992) Macromolecules 25:27 (b) Chujo Y, Tomita I, Saegusa T (1993) Polym Bull 31:553 (c) Chujo Y, Tomita I, Saegusa T (1993) Polym Bull 31:547 (d) Chujo Y, Tomita I, Saegusa T (1994) Macromolecules 27:6714
4. Chujo Y (1994) J Macromol Sci Pure&Appl Chem A31:1647
5. Chujo Y, Tomita I, Hashiguchi Y, Saegusa T (1991) Macromolecules 24:3010
6. Chujo Y, Tomita I, Hashiguchi Y, Saegusa T (1991) Polym Bull 25:1
7. (a) Pelter A, Smith K, Brown HC (1988) In Borane Reagents ; Academic Press: London P272 and references cited therein. (b) Chujo Y, Tomita I, Saegusa T (1991) Polym Bull 26:165
8. Smith K, Pelter A, Jin Z (1994) Angew Chem Int Ed Engl 33:851
9. Org Synthesis (1973) Coll Vol 5:306