Polymer Bulletin 30, 215–222 (1993)

Polymer Bulletin

Hydroboration of styryl-terminated polystyrene with bifunctional thexylborane

Yoshiki Chujo*, Ikuyoshi Tomita, Tsuyoshi Asano, and Takeo Saegusa*****

Department of Synthetic Chemistry, Faculty of Engineering, Kyoto University, Yoshida, Sakyo-ku, Kyoto 606-01, Japan

Summary

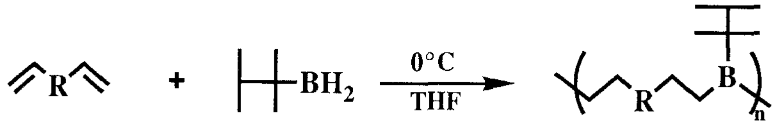
Hydroboration reaction of the terminal double bond of polystyrene with thexylborane gave the polymer bearing one organoboron unit at the center of the polymer, whose molecular weight was found to be doubled in comparison with the starting polymer. The obtained polymer was subjected to the novel polymer reaction with α,α-dichloromethyl methyl ether (DCME) followed by the oxidative treatment. A polymer having one tertiary alcohol unit at the center in the main chain was produced without obvious decrease of the molecular weight.

Introduction

Recently, we explored a novel methodology for the preparation of organoboron polymers in which trialkylborane units were linked in the main chain of the polymer [3-5]. These polymers were produced by the hydroboration polymerization between thexylborane and bifunctional unsaturated compounds such as dienes and diynes (Scheme I). The organoboron polymers thus obtained were examined to be converted to various kinds of functional polymers by the novel polymer reactions which have been reported recently (Scheme II) [6-9]. These polymer reactions show a new synthetic methodology to obtain the various functional polymers whose structures are difficult to build up by the conventional polymer synthetic methods.

Thexylborane has two B-H bonds and generally acts as a bifunctional hydroborane. If hydroboration reaction with this thexylborane is subjected to the terminal double bond of polymers, polymeric

Scheme I



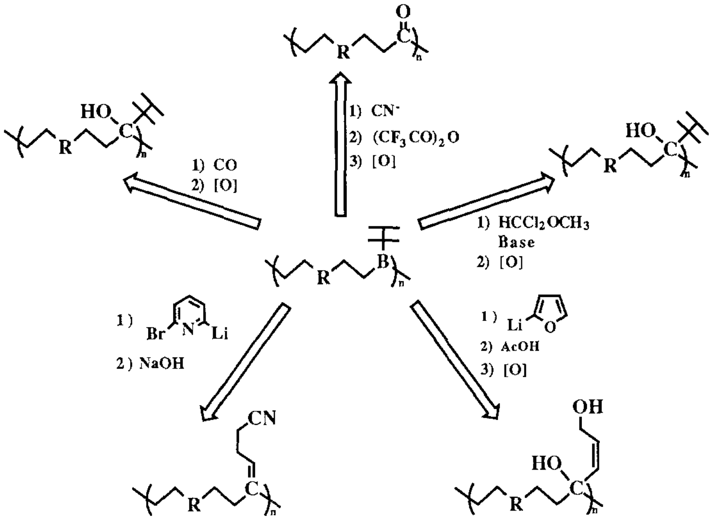
---

*Corresponding author

**See reference 1

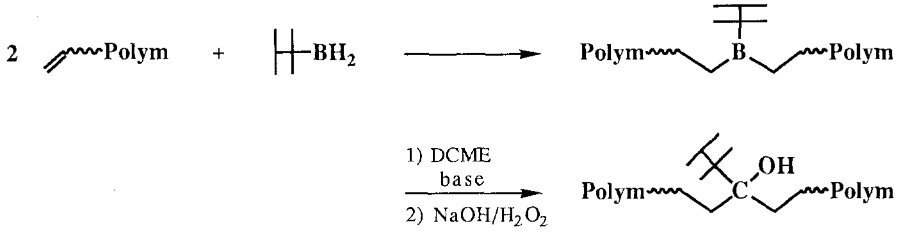
***See reference 2

Scheme II



organoboron species in which only one organoboron unit is located at the center of the main chain can be produced. In the case of anionic living polymerization of polystyrene, end-capping reactions with halosilanes were examined to produce molecular-designed polystyrenes in which the number of the polystyrene arms was successfully controlled [10]. However, the resulting polymers were not examined to be converted to the functional polymers because of the low reactivity of the silicon-carbon bond. The polymers bearing organoboron unit in the main chain of the polymer produced by the present method may have such a potential, since they can be regarded as an organoboron compound having long arms. Thus, the present article describes a novel hydroboration reaction of the terminal double bond of polystyrene and the reaction of the resulting polymer with DCME (Scheme III).

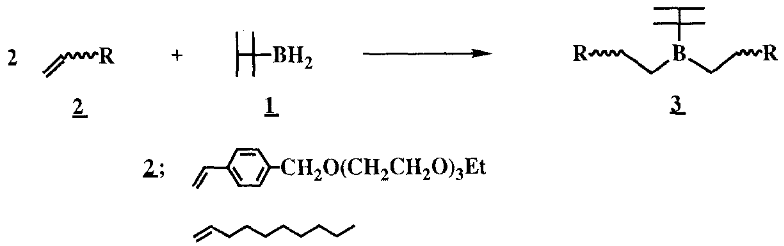
Scheme III



Results and Discussion

As a model reaction for the present study, mono-olefins having relatively longer alkyl chains were first examined. When thexylborane (**1**) was reacted with two molar equivalents of styryl ether (**2**), the resulting organoboron compound (**3**) showed unimodal peak in GPC using dried THF as an eluent (Scheme IV, Figure 1). No peak was detected around that for the starting olefin (**2**). The same result was also obtained from the reaction between 1-decene and **1**. These results show the possibility to obtain the two-armed polymer from **1** and the double bond-terminated polymer.

Scheme IV



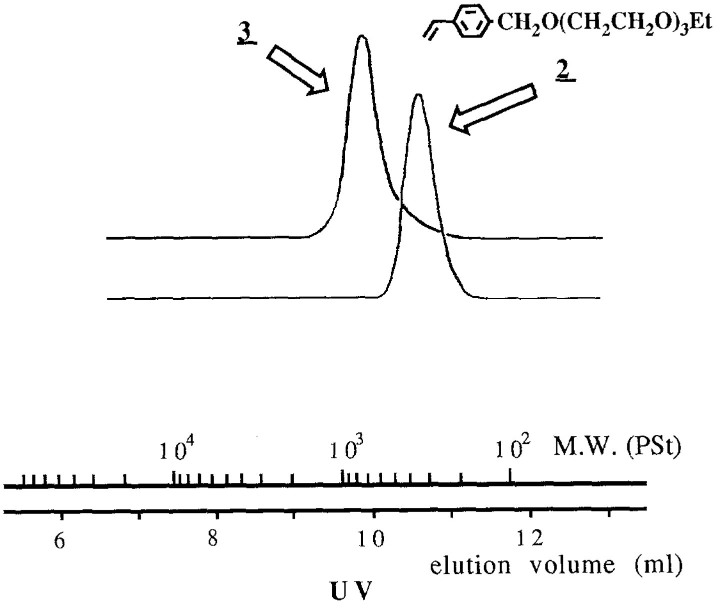
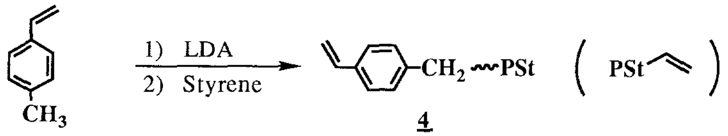


Figure 1 GPC traces of 2 and 3.

Due to the synthetic facility and the high enough functionality, styryl-terminated polystyrene (**4**) obtained by the anionic equilibrium polymerization reported by Nagasaki *et al.* [11] was used for the present study (Scheme V). The obtained **4** was fractionated by the precipitation with methanol/THF system.

Scheme V



When the fractionated **4** was reacted with **1**, the molecular weight of the resulting polymer (**5**) in GPC was found to be shifted to higher molecular weight region. For example, when **4** (M_n=1,130, M_w=2,040) was reacted with **1**, M_n and M_w of the resulting **5** were 2,030 and 3,360, respectively (Figure 2). Although it is difficult to mention that the efficiency of hydroboration reaction was perfect, it is clear that most of the starting polymer was found to be jointed effectively by the thexylborane moiety.

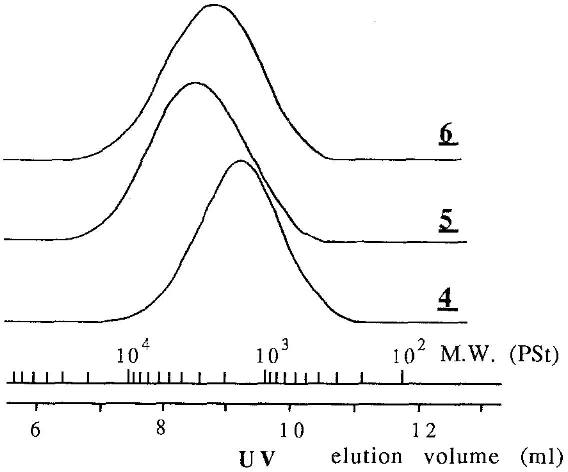
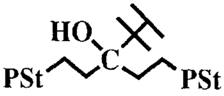


Figure 2 **GPC traces of 4, 5, and 6.**

The obtained polymer having organoboron unit (**5**) was reacted with DCME followed by the oxidation. Without any purification such as reprecipitation, the peak of the resulting polymer (**6**) in GPC appeared to be a unimodal one, and M_n and M_w of **6** were 1,720 and 2,750, respectively. Though these values are a little bit smaller than those of **5**, it should be noted that most part of polymer having organoboron unit was successfully converted to the polymer having alcohol moiety. Without the migration reaction with DCME, organoboron moiety remained in the polymer chain should be cleaved by the oxidative treatment [8], which should result in the formation of the end-alcohol polymer having the molecular weight similar to **4**. Accordingly, small decrease of molecular weight after the reaction might indicate that the small part of **5** was not incorporated to the migration reaction. The results of hydroboration reaction and of the reaction with DCME are summarized in Table I. IR spectrum of **6** indicated the existence of alcohol moiety in the main chain. In the ^{1}H-NMR spectrum of **6**, small peaks attributable to the thexyl groups were observed. The disappearance of the end-styryl groups in **4** also supports the structure of **6** (Figure 3).

Table I Hydroboration Reaction of Styryl-Terminated Polystyrene with Thexylborane followed by the Reaction with DCME.$^{a)}$

 4		 5		 6	
$\bar{M}_n{}^{b)}$	$\bar{M}_w{}^{b)}$	$\bar{M}_n{}^{c)}$	$\bar{M}_w{}^{c)}$	$\bar{M}_n{}^{b)}$	$\bar{M}_w{}^{b)}$
520	680	930	1,200	900	1,160
1,130	2,040	2,030	3,360	1,720	2,750

a) Hydroboration reaction was carried out at room temperature by the addition of 1 to the THF solution of 4 by using a microfeeder.
b) GPC (THF), polystyrene standard.
c) GPC (dry THF), polystyrene standard.

Though this paper deals only the synthesis and one example of the conversion reactions of polymer having one organoboron moiety in its main chain, there are numerous possibilities to convert to the polymers bearing various kinds of functional groups on the basis of organoboron chemistry. In other words, the present polymer reaction may offer a useful synthetic method for the macromolecular design and synthesis.

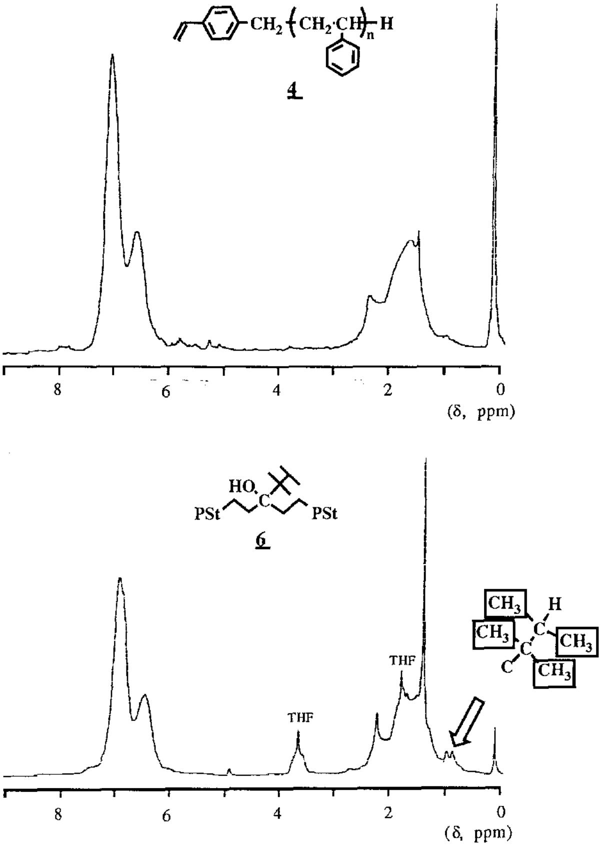


Figure 3 ^{1}H-NMR spectra of 4 and 6.

Experimental Section

Materials and Instruments. Tetrahydrofuran was dried over lithium aluminum hydride and was distilled before use. Thexylborane was prepared from 2,3-dimethyl-2-butene and $Me_2S \cdot BH_3$ as reported earlier [12] and was purified by distillation [3]. Styryl ether (**2**) was prepared from p-chloromethylstyrene, triethylene glycol monoethyl ether, and sodium hydride. 1-Decene was purified by distillation. Styryl-terminated polystyrene was prepared by the reported procedure [11], and was fractionated by the precipitation with methanol/THF followed by the freeze-drying with benzene.

^{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 (Tosoh G3000, THF as an eluent) after calibration with standard polystyrene samples. For the GPC measurements of **3** and **5**, dried THF was used as an eluent with constant nitrogen bubbling.

Synthesis of 3. To a 0.5ml THF solution of styryl ether (**2**, 0.145g, 0.49mmol), **1** (0.026g, 0.26mmol) was added by using a microfeeder (15μmol/min) at ambient temperature under nitrogen. After the complete addition of **1**, the reaction mixture (**3**) was stirred for 1 hour and was subjected to the GPC measurement.

Hydroboration of Styryl-Terminated Polystyrene (4). To a 1ml THF solution of **4** (0.203g, M_n=1,130, 0.18mmol), **1** (0.012g, 0.12mmol) was added by using a microfeeder (15μmol/min) at ambient temperature under nitrogen. After the addition of **1** was over, the reaction mixture (**5**) was stirred for 1 hour and was subjected to the GPC measurement.

The Reaction of 5 with DCME. To a THF solution of **5** prepared by the procedure described above, DCME (0.045g, 0.39mmol) and Et_3COLi in *n*-hexane (1.36N, 0.4ml, 0.54mmol) was added at 0°C, and the reaction mixture was kept stirring overnight. After the oxidative treatment with $NaOH/H_2O_2$ at 50°C for 3 hours, the obtained reaction mixture was extracted with three 20ml portions of THF. When the obtained polymer was precipitated into methanol, 0.192g of **6** was isolated as a white solid.

References and Notes

1. Present address: Research Laboratory of Resources Utilization, Tokyo Institute of Technology, Nagatsuda, Midori-ku, Yokohama 227, Japan.
2. Present address: Kansai Research Institute, International, Chudoji, Minami-machi, Shimogyo-ku, Kyoto 600, Japan.
3. Y. Chujo, I. Tomita, Y. Hashiguchi, H. Tanigawa, E. Ihara, and T. Saegusa, *Macromolecules*, **24**, 345 (1991).
4. Y. Chujo, I. Tomita, Y. Hashiguchi, and T. Saegusa, *Macromolecules*, **25**, 33 (1992).
5. Y. Chujo, I. Tomita, and T. Saegusa, *Polym. Bull.*, **27**, 375 (1992).
6. Y. Chujo, I. Tomita, Y. Hashiguchi, and T. Saegusa, *Macromolecules*, **24**, 3010 (1991).
7. Y. Chujo, I. Tomita, Y. Hashiguchi, and T. Saegusa, *Polym. Bull.*, **25**, 1 (1991).

8. Y. Chujo, I. Tomita, and T. Saegusa, *Polym. Bull.*, **26**, 165 (1991).
9. Y. Chujo, M. Morimoto, and I. Tomita, *Polym. Bull.*, in press (1992).
10. R. W. Pennisi and L. J. Fetters, *Macromolecules*, **21**, 1094 (1988).
11. Y. Nagasaki and T. Tsuruta, *Makromol. Chem.*, **187**, 1583 (1986).
12. H. C. Brown, A. K. Mandal, and S. U. Kulkarni, *J. Org. Chem.*, **42**, 1392 (1977).

Accepted December 14, 1992 S