

# Stable organoboron polymers prepared by hydroboration polymerization of diynes with mesitylborane

Y. Chujo\*, Y. Sasaki, N. Kinomura, N. Matsumi

*Department of Polymer Chemistry, Graduate School of Engineering, Kyoto University, Yoshida, Sakyo-ku, Kyoto, 606-8501, Japan*

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## Abstract

Stable organoboron main-chain polymers were prepared by hydroboration polymerization of various diynes with mesitylborane. The polymerization gave selectively monohydroboration products regardless of the bulkiness of mesityl group, and no gelation was observed. In other words, the organoboron polymers having dialkenylborane repeating units in their main-chain were effectively produced. The resulting polymers were found to be more stable toward air-oxidation than the organoboron polymers prepared from hexylborane. The organoboron polymer prepared from diethynylbenzene and mesitylborane was subjected to reaction with iodine to form poly(phenylene–butadienylene). © 2000 Elsevier Science Ltd. All rights reserved.

*Keywords:* Organoboron polymers; Hydroboration polymerization; Mesitylborane

## 1. Introduction

We have recently explored novel methodologies for the preparation of organoboron main-chain polymers [1–3]. These include hydroboration polymerization of dienes [4], diynes [5], bisallenes [6], and dicyano compounds [7], haloboration polymerization of diynes [8] and bisallenes [9], allylboration polymerization [10,11], phenylboration polymerization, and alkoxyboration polymerization [12]. Especially, hydroboration polymerization between dienes and hexylborane gave a novel type of reactive polymers [13]. Thus, various polymers having a wide variety of functional groups such as alcohol [14–17], ketone [18] and cyano groups [19] were obtained by using these organoboron main-chain polymers as polymeric precursors. In the case of hydroboration polymerization of diynes with hexylborane, terminal diyne and internal diyne are known to show quite different polymerization behavior [5]. When a terminal diyne such as 1,7-octadiyne was used as a monomer, a moderate amount of cross-linking reaction took place due to the further hydroboration reaction of the resulting vinylborane units in the main-chain of the polymer. The produced polymer had a highly branched structure. As a result, gelation was observed when an excess amount of hexylborane was used. On the other hand, an internal diyne such as 3,9-dodecadiyne gave monohydroboration product regardless of

bulkiness of borane and no gelation was observed even in the presence of an excess amount of hexylborane. The organoboron polymers prepared by hydroboration polymerization using hexylborane as a monoalkylborane monomer were found to be relatively unstable toward air-oxidation. Here we report stable organoboron polymers prepared by hydroboration polymerization of diynes using mesitylborane (**1**) as a monoalkylborane monomer.

## 2. Experimental section

### 2.1. Materials and instruments

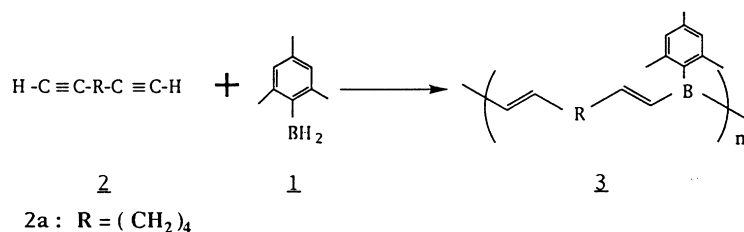
All solvents were dried and distilled before use. Diyne monomers were purified by distillation or recrystallization. <sup>1</sup>H NMR spectra were recorded in CDCl<sub>3</sub> on a JEOL EX-270 instrument (270 MHz). IR spectra were obtained on a Perkin–Elmer 1600 spectrometer. Gel permeation chromatographic (GPC) analyses were carried out on a Tosoh HLC-8020 (TSK gel G3000) and calibrated with polystyrene standards, using dry THF as an eluent under nitrogen.

### 2.2. Hydroboration polymerization of 1,7-octadiyne (**2a**) with mesitylborane (**1**)

A general procedure for the polymerization between **1** and **2a** is described as follows: **2a** was added slowly to a 1.0 M THF solution of **1** at room temperature under nitrogen.

\* Corresponding author. Fax: +81-75-753-5675.

E-mail address: chujo@chujo.synchem.kyoto-u.ac.jp (Y. Chujo).



Scheme 1.

The reaction mixture was stirred at room temperature for 3 h. The product was subjected directly to GPC analysis. As a typical experimental example of polymerization, **2a** (99.8 mg, 0.756 mmol) was added to a 1.0 M THF solution of **1** (76.3 mg, 0.719 mmol) at room temperature under nitrogen. The evaporation of the solvent gave a white solid in a quantitative yield. The obtained organoboron polymer (**3a**) was soluble in common organic solvents such as THF, chloroform and benzene. **3a** could be further purified by reprecipitation from THF solution in dry methanol under nitrogen in 35% yield:  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  0.33–1.79 (–CH<sub>2</sub>, 8H), 1.79–2.63 (–CH<sub>3</sub>, 9H), 6.47–7.03 ppm (C<sub>6</sub>H<sub>2</sub>, –CH=CH, total 6H);  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  21.1, 22.4, 23.2, 26.7, 126.9, 127.5, 127.6, 128.1, 137.7 ppm;  $^{11}\text{B NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  31.7 ppm; IR (KBr)  $\text{cm}^{-1}$  3308 (w), 2902 (m), 2825 (m), 1607 (m), 1556 (m), 1456 (m), 1316 (m), 1261 (m), 1099 (m), 1008 (m), 909 (m), 850 (m), 734 (m), 650 (m).

### 2.3. Hydroboration polymerization of various diynes (**2b–2f**) with **1**

The following organoboron polymers were obtained by using the procedure similar to that described for **3a**. **3b** was prepared from **1** (86.6 mg, 0.656 mmol) and **2b** (76.4 mg, 0.636 mmol) in 39% yield:  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  0.40–1.79 (–CH<sub>2</sub>, 10H), 1.79–2.66 (–CH<sub>3</sub>, 9H), 6.63–7.03 ppm (C<sub>6</sub>H<sub>2</sub>, –CH=CH, total 6H). **3c** was prepared from **1** (107.7 mg, 0.816 mmol) and **2c** (108.3 mg, 0.807 mmol) in 38% yield:  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  0.43–1.82 (–CH<sub>2</sub>, 12H), 1.82–2.63 (–CH<sub>3</sub>, 9H), 6.62–6.94 ppm (C<sub>6</sub>H<sub>2</sub>, –CH=CH, total 6H). **3d** was prepared from **1** (79.5 mg, 0.602 mmol) and **2d** (86.2 mg, 0.531 mmol) in 48% yield:

$^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  0.63–1.91 (–CH<sub>2</sub>, 16H), 1.91–2.60 (–CH<sub>3</sub>, 9H), 6.64–6.96 ppm (C<sub>6</sub>H<sub>2</sub>, –CH=CH, total 6H). **3e** was prepared from **1** (106.3 mg, 0.805 mmol) and **2e** (105.7 mg, 0.788 mmol) in 58% yield:  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  1.07–1.92 (–CH<sub>2</sub>, 8H), 1.92–2.40 (–CH<sub>3</sub>, 15H), 6.00–6.32 ppm (C=CH, 2H). **3f** was prepared from **1** (69.1 mg, 0.523 mmol) and **2f** (97.3 mg, 0.523 mmol):  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  2.14–2.34 (–CH<sub>3</sub>, 9H), 4.61 (–OCH<sub>2</sub>, s, 4H), 6.63–6.97 ppm (C<sub>6</sub>H<sub>2</sub>, C<sub>6</sub>H<sub>4</sub>, –CH=CH, total 10H). **3g** was prepared from **1** (82.7 mg, 0.626 mmol) and **2g** (78.8 mg, 0.625 mmol) in 47% yield:  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  1.97–2.62 (–CH<sub>3</sub>, 9H), 6.41–7.03 (C<sub>6</sub>H<sub>2</sub>, –CH=CH, total 6H), 7.45 ppm (C<sub>6</sub>H<sub>4</sub>, 4H).

### 2.4. Stability of the organoboron polymer (**3a**) toward air-oxidation

The oxidation stability of **3a** in air was examined by monitoring the change of the GPC curve during an oxidation experiment in which a stream of air was bubbled into a CH<sub>2</sub>Cl<sub>2</sub> solution of **3a** at room temperature. After the designated time, the resulting polymer was characterized by GPC analysis (Fig. 3).

### 2.5. Reaction of the organoboron polymer (**3g**) with iodine

To a THF solution of **3g** prepared from 1,4-diethynylbenzene (**2g**) (27.6 mg, 0.219 mmol) and **1** (28.9 mg, 0.219 mmol), were added water (1 ml), sodium acetate (37.7 mg, 0.460 mmol) in methanol (1.5 ml) and methanol (4 ml) solution of iodine (51.5 mg, 0.203 mmol) at 0°C under nitrogen. After the mixture was stirred for 1 day,

Table 1  
Polymerization between **1** and **2a**

Run	Solvent <sup>a</sup>	Temp. (°C)	$M_n^b$	$M_w^b$	Yield (%) <sup>c</sup>
1	THF	RT	5600	9600	35
2	THF	50	4200	5900	63
3	CH <sub>2</sub> Cl <sub>2</sub>	RT	4700	8100	56
4	Benzene	RT	510	910	– <sup>d</sup>
5	CDCl <sub>3</sub>	RT	12 600	28 600	80

<sup>a</sup> [MesBH<sub>2</sub>]: 1.0 M.

<sup>b</sup> GPC (THF), polystyrene standard.

<sup>c</sup> Isolated yields after reprecipitation in MeOH.

<sup>d</sup> Not determined.

Table 2

Dependence of molecular weight on the feed ratio of **1/2a** (polymerization was carried out by adding **2a** to a 1.0 M solution of **1** in THF at room temperature (RT) under N<sub>2</sub>)

Run	<b>1</b> (mmol)	<b>2a</b> (mmol)	<b>1/2a</b>	$M_n^a$	$M_w^a$
1	0.47	0.74	0.64	750	1300
2	0.59	0.66	0.88	1800	3100
3	1.34	1.37	0.98	4800	7900
4	0.79	0.71	1.12	5000	6900
5	0.76	0.61	1.24	1500	2400
6	0.69	0.50	1.39	1000	1800
7	0.73	0.48	1.52	580	950

<sup>a</sup> GPC (THF), polystyrene standard.

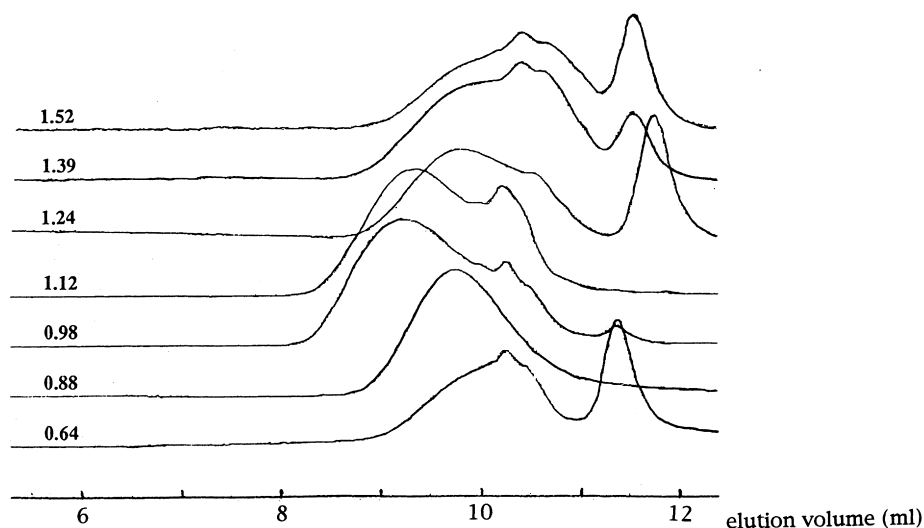


Fig. 1. Dependence of molecular weight of **3a** on the feed ratio of two monomers (**1/2a**).

the reaction was quenched with an excess amount of sodium thiosulfate solution. The polymer was isolated by extracting with diethyl ether followed by precipitation in *n*-hexane. The residual polymer was then dried in vacuo to afford a divinylbenzene polymer (4 g) in 34% yield. The polymer

thus obtained was then subjected to GPC,  $^1\text{H}$  NMR and IR measurements. Yield was 34%:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  6.47–7.71 ppm ( $\text{C}_6\text{H}_4$ ,  $-\text{CH}=\text{CH}$ , total 8H); IR (KBr)  $\text{cm}^{-1}$  3424 (m), 2963 (m), 2360 (s), 2342 (s), 1619 (w), 1558 (w), 1508 (w), 1261 (m), 1092 (m), 1032 (m).

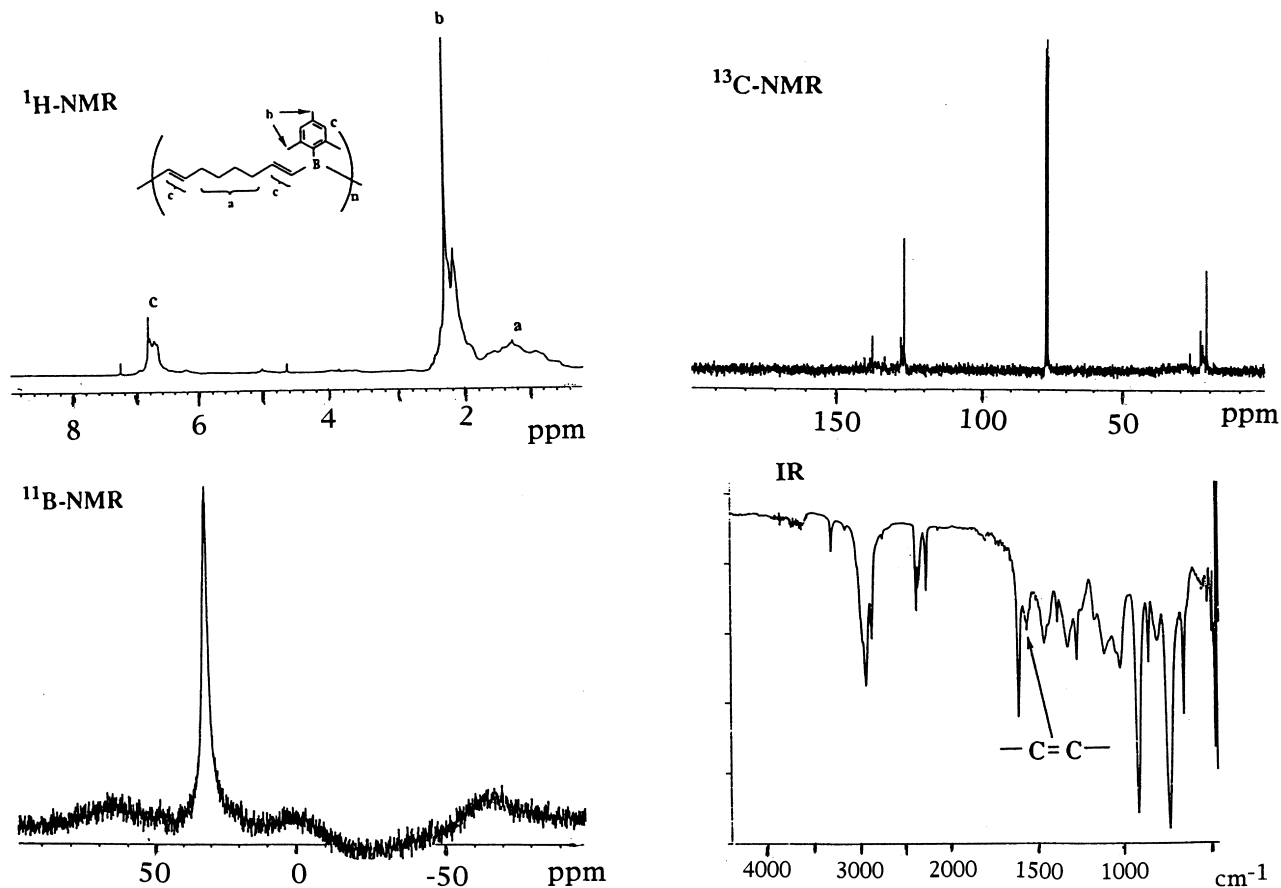
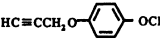
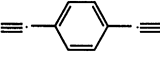
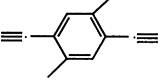


Fig. 2.  $^1\text{H}$ ,  $^{11}\text{B}$ ,  $^{13}\text{C}$  NMR and IR spectra of organoboron polymer **3a**.

Table 3

Hydroboration polymerization between mesitylborane and various diynes (polymerization was carried out by adding a small excess of dienes to a 1.0 M solution of **1** in THF at room temperature under N<sub>2</sub>)

Run	Diyne	<i>M<sub>n</sub></i> <sup>a</sup>	<i>M<sub>w</sub></i> <sup>a</sup>	Yield (%) <sup>b</sup>
1	$\equiv\text{---}(\text{CH}_2)_4\text{---}\equiv$ ( <b>2a</b> )	6500	10 300	35
2	$\equiv\text{---}(\text{CH}_2)_5\text{---}\equiv$ ( <b>2b</b> )	7100	13 200	39
3	$\equiv\text{---}(\text{CH}_2)_6\text{---}\equiv$ ( <b>2c</b> )	6300	12 600	38
4	$\equiv\text{---}(\text{CH}_2)_8\text{---}\equiv$ ( <b>2d</b> )	6100	13 400	48
5	$\text{MeC}\equiv\text{C}(\text{CH}_2)_4\text{C}\equiv\text{CMe}$ ( <b>2e</b> )	2500	3800	58
6	 ( <b>2f</b> )	810	1270	NA <sup>c</sup>
7	 ( <b>2g</b> )	10 500	24 400	47 <sup>d</sup>
8	 ( <b>2h</b> )	–	–	NA <sup>e</sup>

<sup>a</sup> GPC (THF), polystyrene standard.

<sup>b</sup> Isolated yields after reprecipitation in MeOH.

<sup>c</sup> Not isolated.

<sup>d</sup> Isolated yields after reprecipitation in hexane.

<sup>e</sup> No polymerization was observed.

### 3. Results and discussion

1,7-Octadiyne (**2a**) was used as a typical terminal diyne monomer (Scheme 1). Time–conversion analysis was carried out in hydroboration polymerization using **1** and **2a**, from which the reaction was found to be completed within 3 h. The polymerization was carried out under various conditions. The evaporation of the solvent gave a white solid in a quantitative yield. The obtained organoboron polymer (**3a**) was soluble in common organic solvents such as THF, chloroform and benzene. After reprecipitation in dry methanol under nitrogen, GPC measurements were performed. The results are summarized in

Table 1. When the polymerization was carried out at 50°C in THF, the molecular weight of the polymer obtained was relatively low (run 2). When CDCl<sub>3</sub> was used as a solvent, the molecular weight and the yield of the polymer were much higher (run 6). On the other hand, in benzene, only low molecular weight oligomers were obtained (run 4).

The stoichiometry of the employed two monomers should be quite important in a polyaddition reaction. The hydroboration polymerization was carried out by changing the feed ratio of **1** to **2a**. The reaction condition was fixed at room temperature and **2a** was added to a 1.0 M solution of **1**. The results are summarized in Table 2 and Fig. 1. The molecular weight reached a maximum when the feed ratio of two monomers came to unity. Over unity, the molecular weight of the resulting polymer decreased, but no gelation was observed. This result was in sharp contrast to the case of hydroboration polymerization of **2a** with hexylborane, which caused gelation [5]. The present dependence on the feed ratio was quite similar to the results of hydroboration polymerization of dienes [4].

The structure of the organoboron polymer obtained from **1** and **2a** was supported by spectroscopic analyses (Fig. 2). It should be noted that the structure of the organoboron polymer obtained did not change during the reprecipitation in methanol. From the <sup>1</sup>H NMR spectrum, all protons could be assigned to the structure of **3a**. The <sup>11</sup>B NMR spectrum showed only one peak at 22.4 ppm. This result indicates that the addition of **1** to **2a** proceeded in a highly regioselective manner and in a sequential fashion. The chemical shift was found to be lower than that of the organoboron polymer prepared from dienes. This could be due to the shielding effect of π-electron from C=C bonds adjacent to the boron atom. The IR spectrum of the polymer showed the absorption band assignable to C=C bond which was also supported by <sup>1</sup>H and <sup>13</sup>C NMR.

Similarly to **2a**, various diynes were also examined in

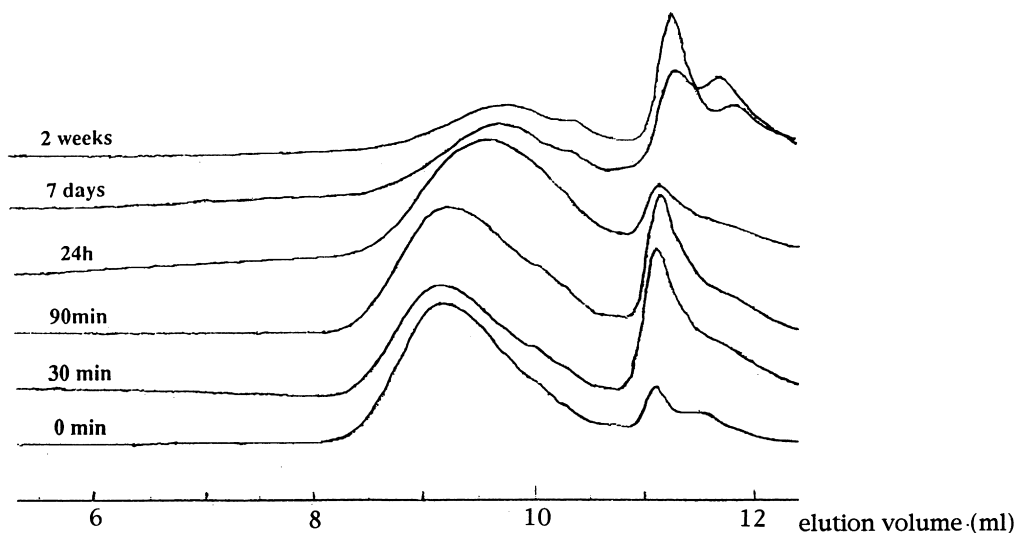
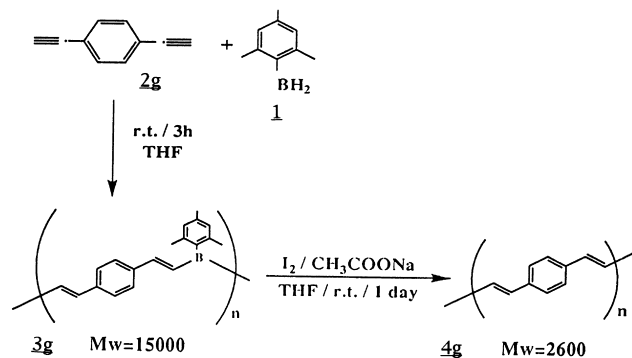


Fig. 3. GPC traces in air-decomposition of **3a**.



Scheme 2.

hydroboration polymerization by using a small excess amount of **1**. As a diene monomer, relatively longer chain diynes were used to avoid the competitive cyclization reaction. The results are summarized in Table 3. Terminal diynes (**2a–2d**), internal diyne (**2e**), ether diyne (**2f**) and aromatic diyne (**2g**) gave the corresponding organoboron polymers. The obtained polymers were white solids and soluble in common organic solvents such as THF, chloroform and benzene. In the case of the internal diyne (**2e**), the molecular weight was relatively lower than those from terminal diynes, probably due to the steric effect. It should be noted that 1,4-diethynylbenzene (**2g**) produced a high molecular weight polymer. The resulting structure (**3g**) has a novel  $\pi$ -conjugation system including C=C bond and phenyl ring via vacant p-orbital of boron atom. This polymer was found to be highly fluorescent with intense blue emissions [20].

Air stability of **3a** was monitored by checking the change of molecular weight in GPC (Fig. 3) after bubbling air through a CH<sub>2</sub>Cl<sub>2</sub> solution of **3a** at room temperature. As shown in Fig. 3, no decrease of the molecular weight was observed even after 90 min. After air-bubbling for two weeks, a little decomposition was observed. This result strongly shows that **3a** is stable enough to be handled under air. This stability might be derived from the steric hindrance of mesityl group, which prevents the attack of oxygen to boron atom. A similar behavior was observed in the organoboron polymers prepared by hydroboration polymerization of bisallene compounds [6].

The organoboron polymers obtained have dialkenylphenylborane repeating units in the main-chain. As a typical reaction of such a dialkenylborane structure, the reaction with iodine [21] was applied to the present polymer system. To a THF solution of **3g** prepared by hydroboration polymerization between **1** and **2g**, iodine and sodium acetate

were added at room temperature and the resulting mixture was stirred for 1 day (Scheme 2). The structure of the obtained polymer was supported by <sup>1</sup>H NMR and IR spectra. In the IR spectrum, the characteristic absorption due to conjugate diene structure was observed at 1565 cm<sup>-1</sup>. However, an obvious decrease in the molecular weight was observed from the result of GPC. This might be due to some side reactions such as chain termination instead of chain recombination after boron cleavage.

#### 4. Conclusions

Mesitylborane was used as a borane monomer in the hydroboration polymerization of various diynes resulting in the formation of air-stable organoboron polymers. The polymers obtained consist of dialkenylmesitylborane repeating units in the main chain. Especially, in the case of hydroboration polymerization of aromatic diynes, a novel  $\pi$ -conjugated organoboron polymer was obtained. This new  $\pi$ -conjugation system including electron deficient boron atom should be our next research target.

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