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Stable organoboron polymers prepared by hydroboration polymerization of dienes with tripylborane

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Summary

Hydroboration polymerization between diene monomers and 2,4,6-triisopropylphenylborane (tripylborane) gave organoboron main-chain polymers. The polymerization was carried out by adding a diene monomer to a THF solution of tripylborane at room temperature under nitrogen. The obtained polymers were found to be more stable compared with the polymers prepared from thexylborane or mesitylborane.

Introduction

We have explored novel methodologies for the synthesis of organoboron main-chain polymers by hydroboration polymerization of dienes [1], diynes [2], bisallenes [3] and dicyano compounds [4]. Especially, the polymers prepared by hydroboration polymerization between dienes and thexylborane are regarded as a novel type of reactive polymers [5], and can be converted to poly(alcohol) [6], poly(ketone) [7] and so on. However, these polymers were not so stable under air, and their decomposition started in a few minutes and was completed in thirty minutes during the air bubbling into the polymer solution [1].

Recently, we have prepared organoboron polymers by hydroboration polymerization between dienes and 2,4,6-trimethylphenylborane (mesitylborane) [8]. These polymers were more stable compared with the polymers prepared from thexylborane. This stability is probably derived from the steric hindrance of mesityl group, which may prevent an attack of oxygen to boron atom. In this paper, we report more stable organoboron polymers prepared by hydroboration polymerization of dienes using 2,4,6-triisopropylphenylborane (tripylborane) as a borane monomer.

Results and discussion

Hydroboration polymerization of diene monomers with tripylborane

Hydroboration polymerization of 1,7-octadiene (**1a**) or 1,9-decadiene (**1b**) was studied (Scheme 1). We have already reported the polymerization using mesitylborane [8]. The optimized polymerization condition was that a diene monomer was added to

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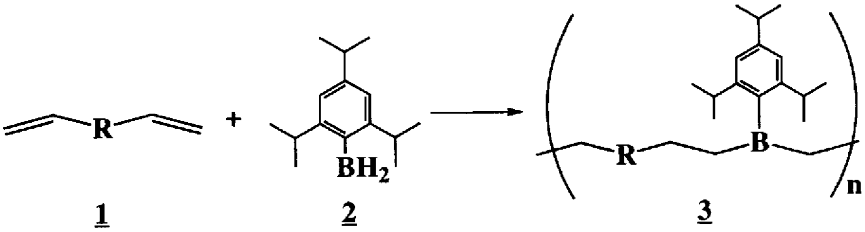
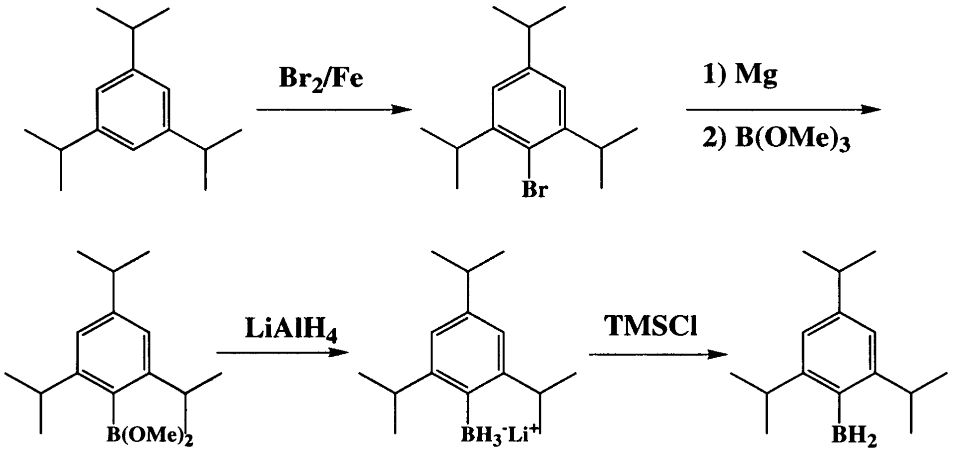
a THF solution of a slightly excess amount of mesitylborane at room temperature under nitrogen and the reaction mixture was stirred for 2 days. Here, the hydroboration polymerization with tripylborane was carried out by using this optimized polymerization condition.



a: R= $(CH_2)_4$
b: R= $(CH_2)_6$

Scheme 1

Tripylborane (2) was prepared according to the reported procedure as shown in Scheme 2. As a typical procedure, hydroboration polymerization between diene and tripylborane was examined as follows. To a THF solution of a slightly excess amount of tripylborane, 1a or 1b was added dropwise under nitrogen at room temperature. After the reaction mixture was stirred for 2 days, the obtained polymer was purified by reprecipitation into methanol to give a polymer as a colorless gum.



Scheme 2

Table 1 summarizes the molecular weights of the obtained polymers (3a) in various concentrations of the reaction mixtures. In the case of the polymerization using thexylborane [1] or mesitylborane [8], the reactions were carried out in 1.0 M THF solutions. However, the polymers with the highest molecular weight were obtained in 0.5 M THF solutions when tripylborane was used. This is probably due to the lower solubility of tripylborane. In addition, the molecular weight and the yield of these polymers were somewhat lower than those of the polymers prepared from mesitylborane. This result might be explained by the lower reactivity of tripylborane derived from more hindered structure. In the case of 3b (Table 2), the molecular weight was found to be 2500 under the optimized polymerization condition.

Table 1. Hydroboration Polymerization between 1a and 2[a)]

Run	[TripBH$_2$]	M_n[b)]	M_w[b)]	M_w/M_n[b)]	Yield (%)[c)]
1	0.2	800	1400	1.8	44
2	0.5	1900	2900	1.5	44
3	1.0	1400	2500	1.8	34

a) Reactions were carried out in THF at room temperature.
b) GPC (THF) polystyrene standards.
c) Isolated yield after reprecipitation into methanol.

Table 2. Hydroboration Polymerization between 1b and 2[a)]

Run	[TripBH$_2$]	M_n[b)]	M_w[b)]	M_w/M_n[b)]	Yield (%)[c)]
1	0.2	1100	2100	1.9	58
2	0.5	2500	4200	1.7	60
3	1.0	1400	2800	1.9	48

a) Reactions were carried out in THF at room temperature.
b) GPC (THF) polystyrene standards.
c) Isolated yield after reprecipitation into methanol.

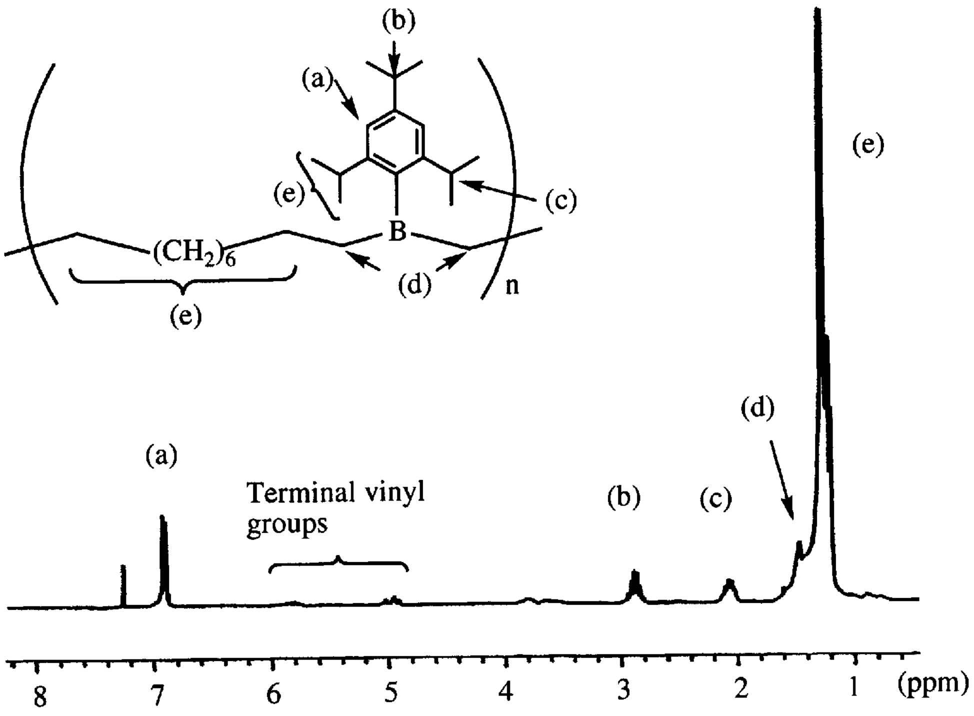


Figure 1. ^{1}H-NMR spectrum of 3b

Characterization of the organoboron polymers

The structures of the organoboron polymers were supported by spectroscopic analyses. From the ^{1}H-NMR spectrum (Figure 1, in $CDCl_3$), all protons could be assigned to the structure of **3b**. In addition, the protons of unreacted terminal vinyl group were detected. The ^{11}B-NMR spectrum of **3b** showed only one peak at 33.7 ppm.

Stability of the organoboron polymer toward air oxidation

Air stability of the organoboron polymer was monitored by checking the change of the molecular weight in GPC after air bubbling into a THF solution of **3a** at room temperature. The result is shown in Figure 2. No decrease of the molecular weight of the peak top in GPC curve (M_p=2100) was observed in a few hours, but a minor peak appeared in a lower molecular weight region. After 24 hours, the polymer showed a slight decrease of the molecular weight (M_p=1800), and the peak in a lower molecular weight region became larger. The polymer prepared from thexylborane began to decompose in a few minutes and the molecular weight was degraded to several hundreds in 30 minutes in an air bubbling experiment. In the case of the polymer obtained from mesitylborane, however, the decomposition was much slower. It took 24 hours in that polymer to degrade the molecular weight to several hundreds. From these results, the polymer prepared from tripylborane was found to be more stable. This stability might be derived from the steric hindrance of bulkier tripyl group, which prevents the attack of oxygen to boron atom.

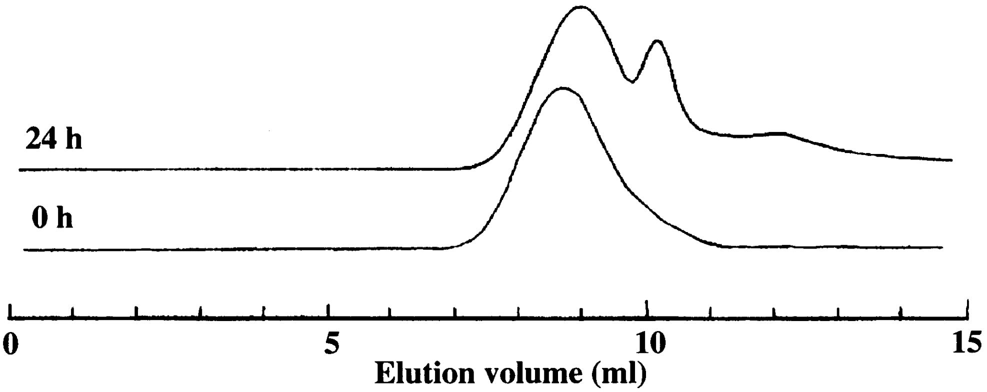


Fig 2. GPC traces of 3a before and after air-bubbling.

Conclusion

Hydroboration polymerization of diene compounds using tripylborane gave air-stable organoboron polymers. Though these polymers decomposed slightly during air-bubbling experiment, they were found to be more stable than the polymers prepared from thexylborane or mesitylborane. From these results, it might be expected that a novel type of stable organoboron materials are obtained by hydroboration polymerization of various diene compounds with tripylborane.

Experimental Section

Materials and instruments

All solvents were dried and distilled before use. 1,7-Octadiene and 1,9-decadiene were purified by distillation. Tripylborane was prepared according to the reported method [9]. ^{1}H-NMR and ^{11}B-NMR spectra were recorded in $CDCl_3$ on a JEOL EX-270 instrument (270 MHz). Gel permeation chromatographic (GPC) analyses were carried out on a Tosoh HLC-8020 (TSK gel G3000) by using THF as an eluent after calibration with polystyrene standards.

*Hydroboration polymerization of 1,9-decadiene (**1b**) and tripylborane (**2**)*

A general procedure for the polymerization between a diene and tripylborane (**2**) is described as follows: The diene was added dropwise to a THF solution of a slightly excess of **2** at room temperature under nitrogen. The reaction mixture was stirred at room temperature for 2 days. After evaporation of the solvent, the polymer was purified by reprecipitation into dry methanol under nitrogen. The obtained polymers were soluble in common organic solvents such as THF, chloroform and benzene.

As a typical example of polymerization, **1b** (186 mg, 1.35 mmol) was added to a 0.5 M THF solution of **2** (305 mg, 1.41 mmol). After purification, the polymer was obtained in 60 % yield. ^{1}H-NMR ($CDCl_3$) δ 1.19-1.46 (CH_3 (tripyl), CH_2), 1.60 (B-CH_2), 2.07 (CH (tripyl)), 2.89 (CH (tripyl)), 6.92 (Ar). ^{11}B-NMR ($CDCl_3$) δ 33.7.

Air stability of the organoboron polymer

The oxidation stability of the polymer was examined by monitoring the change of the GPC curve during an oxidation experiment in which a stream of air was bubbled into a THF solution of **3a** at room temperature. After the designated time, the resulting polymer was characterized by GPC analysis.

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For the synthesis of 2-tripylbromide, see Whitesides G M, Eisenhut M, Bunting W M (1974) J Am Chem Soc 96: 5398