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Hydroboration polymerization of dicyano compounds

II. Reactions of isophthalonitrile with primary or secondary alkylborane

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Summary

The steric effects of the alkyl substituents on the monoalkylborane monomers in hydroboration polymerization of dicyano compounds were examined. *t*-$BuBH_2$•NMe_3 gave the corresponding poly(cyclodiborazane)s by the reaction with aromatic dicyano compounds such as terephthalonitrile or isophthalonitrile. When less sterically hindered *n*-$BuBH_2$•NMe_3 was used as a monomer, the polymerization with isophthalonitrile resulted in gelation due to the further hydroboration reaction of initially formed iminoborane species. On the other hand, *i*-$PrBH_2$•NMe_3 gave the soluble polymers, which showed, however, lower molecular weights in comparison with those from *t*-$BuBH_2$•NMe_3. From these results, hindered alkyl groups in monoalkylboranes were found to play an important role to prevent side reactions in hydroboration polymerization of dicyano compounds.

Introduction

Recently, we have reported the synthesis of novel boron-containing polymers consisting of boron-nitrogen four-membered rings (cyclodiborazane units) by the reaction between dicyano compounds and *t*-$BuBH_2$•NMe_3 (**1a**) [3]. As shown in Scheme I, the formation of intermediate iminoborane species, which dimerize to construct a cyclodiborazane unit, should be essential for this polymerization. The obtained polymers showed high stability toward air and moisture. In this hydroboration polymerization, aromatic dicyano monomers such as isophthalonitrile or terephthalonitrile gave polymers having desired structures. On the other hand, aliphatic dicyano compounds (α,ω-dicyanoalkanes) gave only the corresponding oligomers due to the further hydroboration reaction of the iminoboranes. In these cases, B-H species attack the iminoborane species to form dibora-amine units, which causes the scission of polymeric chain or sometimes gelation. These results may indicate that the sufficient reactivity as well as selectivity between hydroboration and dihydroboration (i.e., attacks of B-H towards iminoborane species) are required for the synthesis of poly(cyclodiborazane)s. If less sterically hindered monoalkylboranes are used as monomers, the iminoboranes generated in this reaction might be easily attacked by another borane to produce dibora-amines which may prevent the high polymerization or may cause a gelation. In order to clarify this explanation, hydroboration polymerizations of

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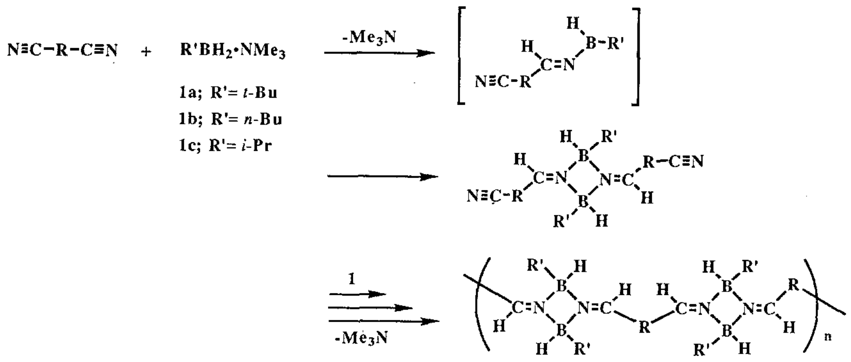
Footnotes 1 and 2, see references

dicyano compounds with less sterically hindered *n*-$BuBH_2 \cdot NMe_3$ (**1b**) and *i*-$PrBH_2 \cdot NMe_3$ (**1c**) were carried out here.

Scheme I



Results and Discussion

Monoalkylboranes having bulky alkyl substituents are known to be handled without decomposition, while those with smaller substituents are usually unstable to be decomposed to the disproportionated products [4]. On the other hand, monoalkylborane-amine complexes are known to be a good candidate to generate the corresponding free monoalkylboranes *in situ* by the thermal dissociation of amine ligand [5]. Therefore, monoalkylborane-trimethylamine complexes such as *n*-$BuBH_2 \cdot NMe_3$ (**1b**), and *i*-$PrBH_2 \cdot NMe_3$ (**1c**) were used in the present hydroboration polymerization.

Table I. Hydroboration polymerization of isophthalonitrile (2) with *n*-$BuBH_2 \cdot NMe_3$ (1b).[a]

Run	$\frac{[n\text{-}BuBH_2]}{[CN]}$ Ratio	Condition		$\overline{M}_n$[b]	$\overline{M}_w$[b]
1	0.51	100°C	1h	1,150	1,560
2	0.95	100°C	1h	-[c]	-[c]
3	1.67	100°C	1h	-[c]	-[c]
4	1.05	80°C	1h	590	1,120
5	1.05	80°C	2h	860	2,910
6	1.05	80°C	4h	1,010[d]	15,600[d]

a) Reactions were carried out in diglyme under nitrogen.

b) Estimated by GPC (polystyrene standards).

c) Gelation was observed during polymerization.

d) Some part of reaction mixture became insoluble in THF.

Hydroboration Polymerization of Isophthalonitrile (2) with *n*-$BuBH_2$•NMe_3 (1b). Hydroboration polymerization of isophthalonitrile (2) with *n*-$BuBH_2$•NMe_3 (**1b**) was carried out in diglyme. Table I summarizes the results of the effects of feed ratio (**1b**/**2**) and temperature. When two molar equivalent of **1b** (i.e., equimolar amount for the nitrile group) was added to **2**, a gelation was observed before complete addition of **1b** (Run 2). A half molar of **1b** gave the soluble oligomer, however, the molecular weight was only around one thousand (Run 1). Under the milder condition (i.e., at 80°C), the reaction took place very slowly, and a part of the reaction mixture became insoluble after the reaction for 4 hours (Run 6).

The model reaction using benzonitrile (**3**) was carried out under various molar ratios of **1b**/**3**, from which the complete conversion of **3** was observed when nearly two fold excess of **1b** was used (Figure 1). These results may indicate that **1b** does not have sufficient selectivity in hydroboration and dihydroboration. In other words, less sterically hindered **1b** caused the side reactions such as gelation or chain scission due to the attacks of B-H species toward iminoborane species in comparison with more sterically *t*-$BuBH_2$•NMe_3 (**1a**).

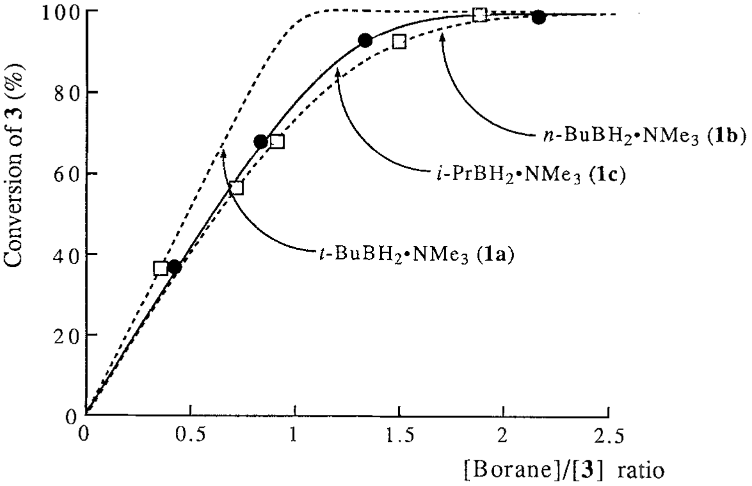


Figure 1. GC conversion curves of **3** by the reaction with **1a**, **1b** (□), or **1c** (●).

Hydroboration Polymerization of Isophthalonitrile (2) with *i*-$PrBH_2$•NMe_3 (1c). Table II summarizes the results of hydroboration polymerization of isophthalonitrile (2) with *i*-$PrBH_2$•NMe_3 (**1c**). As shown in this table, the sufficient reactivity was not obtained at 80°C, and a gelation took place at 120°C. However, no gelation was observed in every feeding ratio of two monomers, when reactions were carried out at 100°C (Table II, Runs 1-5). The molecular weight of the resulting polymer increased with an increase of feed ratio of **1c**/**2**. In ^{1}H-NMR spectrum of the obtained polymer (Run 5), broad peaks at 3.6 and 4.9ppm attributable to the methylene protons adjacent to amino group and those adjacent to bora-amino group, respectively, were observed [6]. Although the polymerization between **1c** and **2** gave a soluble polymer under the examined reaction condition, the structure of the obtained polymer was found to contain primary amines by the attack of B-H bonds towards iminoborane species.

Table II. Hydroboration polymerization of isophthalonitrile (2) with *i*-$PrBH_2$•NMe_3 (1c).[a]

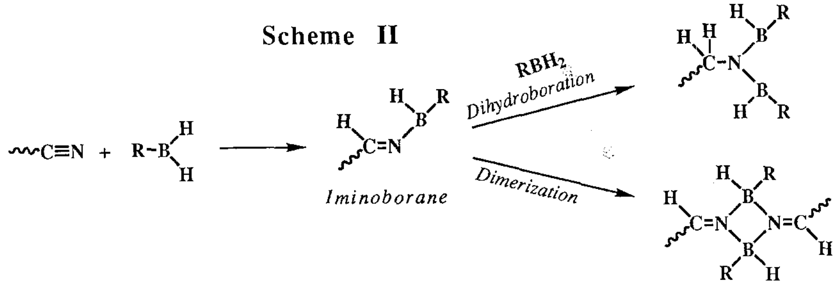
Run	$\frac{[i\text{-PrBH}_2]}{[CN]}$ Ratio	Condition		$\overline{M}_n$[b]	$\overline{M}_w$[b]
1	0.54	100°C	1h	630	1,030
2	0.71	100°C	1h	870	2,410
3	1.10	100°C	1h	950	2,450
4	1.50	100°C	1h	2,430	19,000
5	2.14	100°C	1h	3,040	20,300
6	1.06	80°C	1h	490	650
7	1.06	80°C	2h	590	960
8	1.06	80°C	3h	740	1,500
9	1.07	120°C	1h	gelation	

a) Reactions were carried out in diglyme under nitrogen.
b) Estimated by GPC (polystyrene standards).

When the model reaction of **1c** with **3** was carried out under various feed ratios of **1c**/**3**, the conversion of **3** was found to become closer to the theoretical 1:1 reaction in comparison with that of the reaction with **1b** (Figure 1). However, the complete conversion of **3** was not observed when an equimolar amount of **1c** was used for the reaction, which is rather far different from the result using *t*-$BuBH_2$•NMe_3 (**1a**).

Conclusion. In the present hydroboration polymerization of dicyano compounds, hindered alkyl groups were found to play an important role. As illustrated in Scheme II, there are two possible reactions of the intermediate iminoborane species. The attack of B-H species to C=N bonds by "dihydroboration" forms dibora-amine species. This side reaction causes the chain scission or gelation, which should be undesirable for high polymerization. Another pathway is a "dimerization" of iminoborane species, which gives cyclodiborazane structure as a polymer repeating unit. The latter desired reaction is predominant in the case of *t*-$BuBH_2$•NMe_3 (**1a**) because the attack of **1a** to iminoborane species might be restricted due to steric effect [3]. On the other hand, *n*-$BuBH_2$•NMe_3 (**1b**) is likely to be subjected to side reaction. In the case of i-PrBH$_2$•NMe$_3$ (**1c**) having intermediate steric hindrance, both of these two reactions take place, and as a result, low molecular weight oligomers are obtained.

Scheme II



Experimental Section

Materials and Instruments. n-BuBH$_2$•NMe$_3$ (**1b**) and i-PrBH$_2$•NMe$_3$ (**1c**) were obtained by the reaction of the corresponding trialkylboroxines [7] with lithium aluminum hydride in the presence of trimethylamine as previously described, and were purified by distillation [5]. Isophthalonitrile (**2**) was purified by recrystallization from ethyl acetate. Benzonitrile (**3**) was purified by distillation under reduced pressure.

^{1}H-NMR spectra were recorded in CDCl$_3$ on a Hitachi R-600 instrument (60MHz, tetramethylsilane as an internal standard). IR spectra were obtained on a Perkin Elmer 1600 spectrometer. Gas chromatographic analyses were made on a Simadzu GC-6A instrument. Gel permeation chromatographic analyses were carried out on a Tosoh HLC-8020 (TSK Gel G3000) after calibration with standard polystyrene samples.

Hydroboration Polymerization between 1b and 2. A typical procedure is shown as follows (Table I, Run 1): In a two-way reaction flask equipped with a stirrer tip, a septum inlet, and a reflux condenser with a three-way cock, **2** (0.0623g, 0.486mmol) and diglyme (0.12ml) were introduced under nitrogen. To this solution, **1b** (0.0635 g, 0.492mmol) was added using a microfeeder at 100°C. The reaction mixture was kept stirring for additional 1 hour at that temperature. Diglyme was removed under vacuum and the obtained product was subjected to GPC measurement. Similarly, other experi-ments in Table I (Runs 2-6) were carried out using the following monomer feedings: **2** (0.0611g, 0.477mmol) and **1b** (0.117g, 0.904mmol, Run 2), **2** (0.0631g, 0.492mmol) and **1b** (0.210g, 1.63mmol, Run 3), and **2** (0.0562g, 0.439mmol) and **1b** (0.119g, 0.920mmol, Runs 4-6), respectively.

Model Reaction of 1b with 3. To a nitrogen-replaced two-way flask containing **3** (0.0873g, 0.847mmol), tetradecane (0.040g, as an internal standard), and diglyme (0.2ml), was added **1b** (0.0327g, 0.253mmol, 29.9 mol% of **3**) by using a microfeeder (it required 10 min. for the complete addition) at 100°C. After the reaction for 1hour at 100°C, the conversion of **3** was measured by GC (conversion; 34.4%). Similarly, a series of the experiments were carried out by using the different molar ratios as follows: **3** (0.158g, 1.53mmol) and **1b** (0.133g, 1.03mmol, **1b**/**3**=0.674), **3** (0.0947g, 0.918mmol) and **1b** (0.107g, 0.827mmol, **1b**/**3**=0.901), **3** (0.0742g, 0.720mmol) and **1b** (0.117g, 0.903mmol, **1b**/**3**=1.25), and **3** (0.0874g, 0.848mmol) and **1b** (0.199g, 1.54mmol, **1b**/**3**=1.82), respectively.

Hydroboration Polymerization between 1c and 2. A typical procedure is shown as follows (Table II, Run 1): In a two-way reaction flask equipped with a stirrer tip, a septum inlet, and a reflux condenser with a three-way cock, **2** (0.0450g, 0.327mmol) and diglyme (0.13ml) were introduced under nitrogen. To this solution, **1c** (0.0620g, 0.539mmol) was added using a microfeeder at 100°C. The reaction mixture was kept stirring for additional 1 hour at that temperature. Diglyme was removed under vacuum and the obtained product was subjected to GPC measurement. Similarly, other experiments in Table I (Runs 2-9) were carried out using the following monomer feedings: **2** (0.0509g, 0.397mmol) and **1c** (0.0649g, 0.564mmol, Run 2), **2** (0.0438g, 0.342mmol) and **1c** (0.0868g, 0.755mmol, Run 3), **2** (0.0419g, 0.327mmol) and **1c** (0.113g, 0.980mmol, Run 4), **2** (0.0454g, 0.354mmol) and **1c** (0.175g, 1.52mmol, Run 5), **2** (0.0612g, 0.478mmol) and **1c** (0.116g, 1.01mmol, Runs 6-8), and **2** (0.0419g, 0.327mmol) and **1c** (0.0805g, 0.700mmol, Run 9), respectively. Typical spectroscopic data of the polymer (in Table II, Run 5) are shown as follows; ^{1}H-NMR (δ, ppm) 0.36-1.98 (i-C_3H_7, m), 3.6 (-CH_2-N, br, m), 4.9 (-CH_2-N-B, br, m), 7.1-8.6 (C_6H_4, -CH=N, m), (integral ratios; 2.7:0.16:0.13:1); IR (in $CHCl_3$) 2941, 2860, 2358, 1651, 1462, 1097, 1034cm^{-1}.

Model Reaction of 1c with 3. Similarly to the case of model reaction of **1b** with **3**, a series of the experiments were carried out by using the different molar ratios of **1c**/**3** as follows: **3** (0.108g, 1.04mmol) and **1c** (0.050g, 0.438mmol, **1c**/**3**=0.421), **3** (0.0914g, 0.886mmol) and **1c** (0.0847g, 0.736mmol, **1c**/**3**=0.831), **3** (0.0766g, 0.743mmol) and **1c** (0.114g, 0.989mmol, **1c**/**3**=1.33), and **3** (0.0687g, 0.666mmol) and **1c** (0.166g, 1.44mmol, **1c**/**3**=2.16), respectively.

References and Notes

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4. Pelter A, Smith K, Brown HC (1988) pp 178 *Borane Reagents*, Academic Press London.
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6. ^{1}H-NMR spectrum of the polymer formed was measured after precipitation with EtOH/H_2O (v/v=1/1). The yield of the obtained product was 139% based on the ideal polymer structure, and the peak for i-propyl group was larger than the expected. Thus, the structure of the polymer should be contaminated with diboraamines as well as free amines.
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