Hydroboration Polymerization of Dicyano Compounds. 4. Synthesis of Stable Poly(cyclodiborazane)s from Dialkylboranes

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ABSTRACT: Dialkylboranes were used as a monomer in hydroboration polymerization of dicyano compounds. The bulk polymerization of $(n\text{-}Bu_2BH)_2$ with α,ω-dicyanoalkanes gave the corresponding poly(cyclodiborazane)s consisting of boron–nitrogen four-membered rings. The obtained polymers were colorless gums and soluble in common organic solvents such as THF or chloroform. The molecular weights of the resulting poly(cyclodiborazane)s were higher than those prepared from monoalkylboranes. Poly(cyclodiborazane)s thus obtained showed a high stability toward air and moisture. The thermal stability was also much improved in comparison with those prepared by hydroboration polymerization of dicyano compounds with monoalkylboranes. After pyrolysis of poly(cyclodiborazane)s, some residue remained. This result indicates a possibility of poly(cyclodiborazane) as a polymeric precursor for the preparation of boron-containing inorganic materials.

Introduction

Recently, we have explored novel methodologies for the preparation of organoboron polymers from dienes or diynes.[3] These organoboron polymers were used as a new type of reactive polymer to give polymers having a wide variety of functional groups.[4] On the other hand, we have also reported the preparation of boron-containing polymers consisting of boron–nitrogen four-membered rings (cyclodiborazane units) (Scheme 1). Hydroboration polymerization of dicyano compounds with monoalkylboranes[5] such as $t\text{-BuBH}_2\cdot\text{NMe}_3$ or allylboration polymerization of dicyano compounds with triallylborane[6] gave the corresponding poly(cyclodiborazane)s. These polymers were also obtained by the condensation reaction of bis(silylimine)s with chlorodialkylboranes or with methyl dialkylborinates.[7] The poly(cyclodiborazane)s were found to be stable toward air and moisture in comparison with organoboron polymers prepared by hydroboration polymerization of dienes and/or diynes.[3] From the results of pyrolysis at 900 °C, the poly(cyclodiborazane)s can be expected as a polymeric precursor for the production of boron-containing inorganic materials.

To the boron atoms in the polymers prepared by hydroboration polymerization of dicyano compounds with monoalkylboranes are attached one alkyl group and one hydride. This structure sometimes causes side reactions such as further hydroboration reaction of B–H species with iminoboranes. As a result, gelation or formation of low molecular weight oligomers was observed in these cases.[5] After heating this polymer at 100 °C, gelation was observed. The poly(cyclodiborazane)s prepared by allylboration polymerization also become insoluble after heating at 100 °C.[6] These cross-linking reactions might be due to further hydroboration or allylboration reaction of B–H or B–allyl groups remaining on the boron atoms in the structure of the polymers.

From the viewpoints of the clarification of polymerization behavior and also of the exploration of much stable poly(cyclodiborazane)s, we examined here hydroboration polymerization of dicyano compounds with dialkylboranes.

Results and Discussion

According to the previous report by Lloyd and Wade,[8] the reaction of dimethylborane or diethylborane (existing as their dimers) with nitriles such as acetonitrile gives the corresponding dimers of iminoboranes (i.e, derivatives of cyclodiborazanes; Scheme 2). In this system, two alkyl groups are attached on the boron atoms in the cyclodiborazane unit, and the products are known to be stable in air. If dialkylboranes are used for the hydroboration polymerization with dicyano monomers, the boron-containing polymers having corresponding structures might be produced. The general scheme of the present hydroboration polymerization is shown in Scheme 3, which includes the plausible polymerization mechanism.

As a dialkylborane monomer, di-n-butylborane (**1**, existing as its dimer) was used here, and the polymerization with adiponitrile (**2c**) was examined at ambient temperature. Among the examined reaction media (e.g., dichloromethane, THF, and without any solvents), the reaction in bulk gave the best result. Although the reaction initially proceeded in a two-phase system, a homogeneous viscous gum was obtained within 1 h.[9] Therefore, the following studies were examined in bulk conditions. As summarized in Table 1, polymerization reactions were carried out by changing the feed ratio of two monomers ([B–H]/[C≡N]) from 0.65 to 2.16.

While the isolated yields of the polymers **3c** (runs 1–4, based on **1**; runs 5–8, based on **2c**) were around 80–90%, the molecular weights of **3c** were largely decreased in the presence of a large excess amount of **1**. The present hydroboration polymerization can be classified as a step-growth polymerization. Accordingly, the molecular weights of the polymers should be effected by the feed ratio of two monomers. However, in the present system, only the excess borane influenced the molecular weight of the resulting polymer. Although there are no evidences to support an idea to explain these phenomena, the observed insensitivity on the feed ratio might be rationally explained if the reaction is supposed to proceed in the borane phase. In the case that an excess amount of **2c** is used for the polymerization, only a small part of **2c** gradually dissolves into the borane phase which participates in polymerization. Thus, an excess amount of **2c** remained unreacted in another phase. On the other hand, in the presence of an excess amount of **1**, the unreacted **1** always exists in the polymerization system, which interrupts polymerization by side reactions such as a second hydroboration toward iminoboranes.

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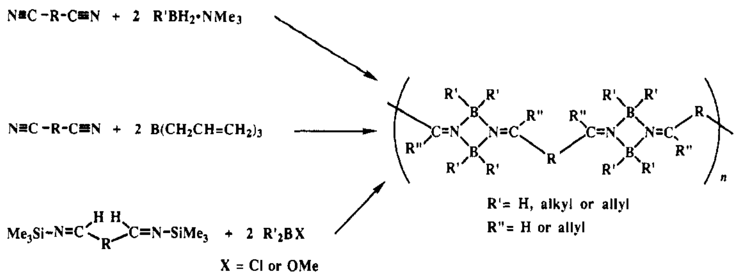
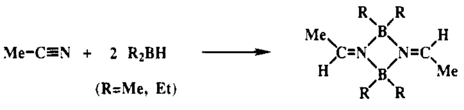
Scheme 1



Scheme 2



Scheme 3

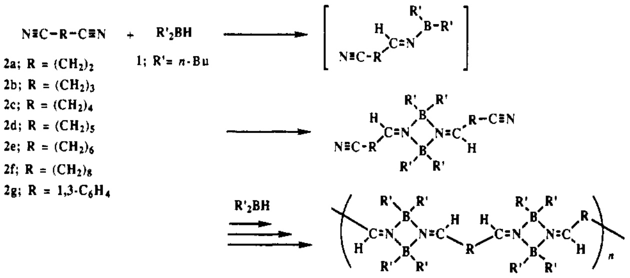


Table 1. Hydroboration Polymerization of Adiponitrile (2c) with Dibutylborane under Varied Feed Ratios[a]

run	[B-H]/[C≡N] ratio	yield[b] (%)	M_n[c]	M_w[c]
1	0.65	91	18 700	46 400
2	0.76	82	22 700	56 400
3	0.83	85	19 100	53 600
4	0.90	78	17 100	51 700
5	1.02	82	16 900	53 700
6	1.10	83	16 100	57 200
7	1.42	79	9 930	29 400
8	2.16	79	910	1 590

[a] Polymerizations were carried out in bulk at room temperature. [b] Isolated yields after precipitation into EtOH/H_2O (v/v, 1/1). Runs 1–4, based on 1; runs 5–8, based on 2c. [c] GPC (THF), polystyrene standards.

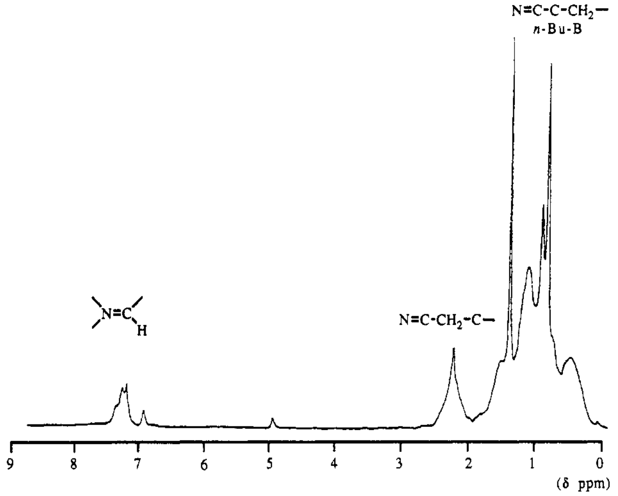


Figure 1. ^1H NMR spectrum of poly(cyclodiborazane) (3c).

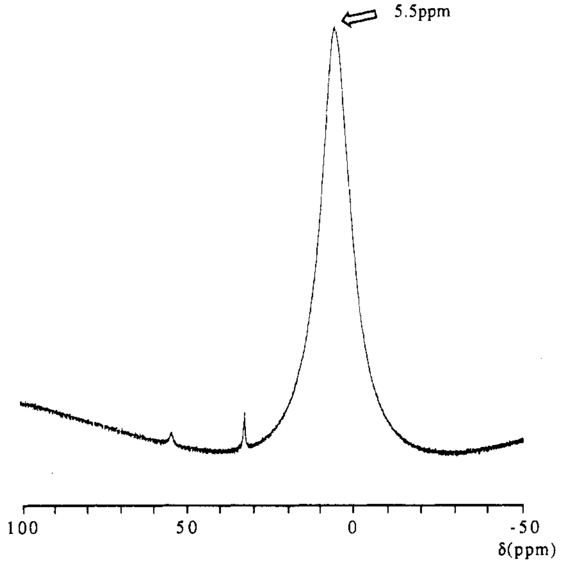


Figure 2. ^{11}B NMR spectrum of 3c.

The structure of the obtained polymer (3c) was confirmed by ^{11}B and ^1H NMR and IR spectra. In the ^1H NMR spectrum, protons of imines, methylenes adjacent to imines, and other protons (inner methylenes and the *n*-butyl group on the boron atom) were observed (Figure 1). The integral ratios of these peaks were in good agreement with the expected structure. In the ^{11}B NMR, a broad peak at 5.5 ppm attributable to the four coordinated boron species (i.e., iminoborane dimers) was observed (Figure 2). In its IR spectrum, an absorption at 1684 cm^{-1} which can be attributed to the iminoborane dimers was observed (Figure 3). The peaks for boron hydride or nitrile were not detected. These results show that 3c does not contain the undesirable structures such as diboraamines as a result of dihydroboration.

Table 2 summarizes the results of polymerizations of 1 with various dicyano compounds (2a–g). In the case of aliphatic dicyano monomers, the corresponding polymers were obtained in high yields. Monomers having longer methylene chains (2e and 2f) produced lower molecular weight polymers in comparison with those having shorter methylenes (2a–d) (runs 5 and 6 vs runs 1–4). In the case of 2e or 2f, dicyanoalkane and 1 dissolved each other to produce a homogeneous system just after the addition of two monomers. These differences should be due to lower polarity in the case of 2e and 2f than in that of 2a–d. It is not clear why the two-phase system is suitable to make polymers having higher molecular weights in the present system. It can be noted that interfacial polycondensation is known to ensure the stoichiometric reaction between two monomers. However, slow addition of the monomer (2e or 2f) using a microfeeder did not give better results. In the case of solid dicyano monomers (2a and 2g), the yields of the resulting polymers were rather low, presumably because polymerizations may proceed to produce viscous gum before the complete reaction of dicyano monomers. Accordingly, polymerization of 2a was carried out above its melting point (70 °C) at the early stage of the reaction to give polymer 3a in high yield (run 1).

The air stability of 3c was demonstrated by checking the change of its molecular weight in GPC after keeping 3c in air for a designated period. The molecular weight

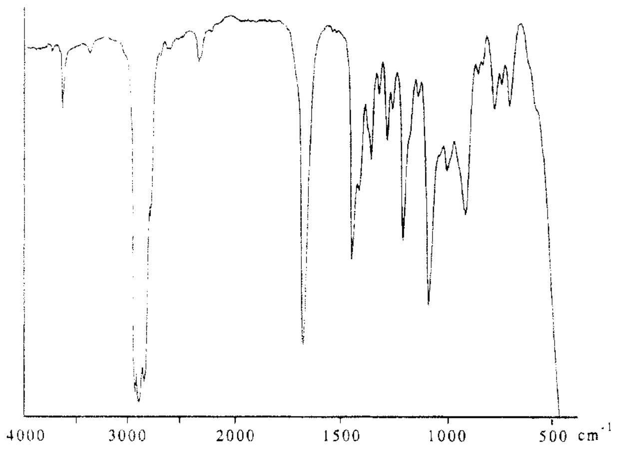


Figure 3. IR spectrum of **3c**.

Table 2. Hydroboration Polymerization of Various Dicyano Compounds with Di-*n*-butylborane (1)[a]

run	dicyano compounds	yield[b] (%)	M_n[c]	M_w[c]
1[d]	$NC(CH_2)_2CN$ (2a)	88	16 800	49 900
2	$NC(CH_2)_3CN$ (2b)	90	10 100	23 500
3	$NC(CH_2)_4CN$ (2c)	78	17 100	51 700
4	$NC(CH_2)_5CN$ (2d)	77	25 000	69 900
5	$NC(CH_2)_6CN$ (2e)	76	3 080	5 830
6	$NC(CH_2)_8CN$ (2f)	88	5 930	9 070
7	*m*-$NC\text{-}C_6H_4\text{-}CN$ (2g)	25	3 540	14 700

[a] Polymerizations were carried out in bulk at room temperature. [b] Isolated yields after precipitation into $EtOH/H_2O$ (1/1). [c] GPC (THF), polystyrene standards. [d] Polymerization was carried out at 70 °C for 30 min and then at room temperature for 2 h.

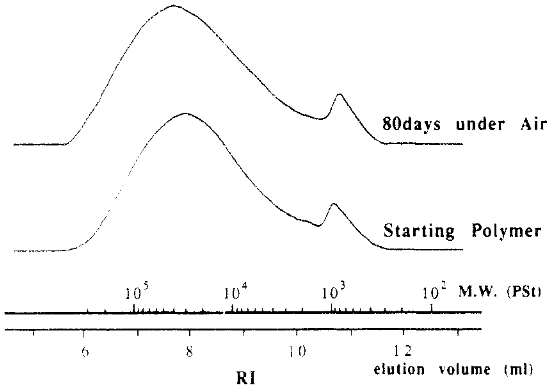


Figure 4. GPC traces for **3c** (just after preparation) and the sample after keeping it in air at room temperature for 80 days.

and the molecular weight distribution of the sample after keeping it for 80 days in air were the same in comparison with those of the sample just after polymerization (Figure 4). The minor peak in the low molecular weight region in Figure 4 might be due to cyclic oligomers. IR and ^1H NMR spectra of the sample after storage were identical with those of the sample just after preparation. Therefore, this boron-containing polymer was concluded to be stable in air.

Thermogravimetric analysis of **3c** was carried out under nitrogen to demonstrate the possibility as a precursor providing inorganic boron-containing materials. As shown in Figure 5, the weight loss started around 140 °C and was completed around 700 °C. After the measurement of TGA, about 12% of a residue remained as a black solid. In the DSC measurement, no specific peaks were detected below 140 °C.

The molecular weight of the sample after heating at 140 °C and at 200 °C was somewhat decreased as shown in Figure 6. On the other hand, the minor peak assignable to cyclic oligomers slightly increased after heating. These results might be due to thermal decomposition and/or cyclization. However, they were still soluble in organic solvents, which is completely different from the case of the polymer prepared from monoalkylborane.[5] This better thermal stability might be due to the absence of a boron hydride moiety in the polymer chain prepared from dialkylboranes. That is, polymers from dialkylborane do not have any reactive groups on the boron atom which improved the thermal stability of the boron-containing polymers.

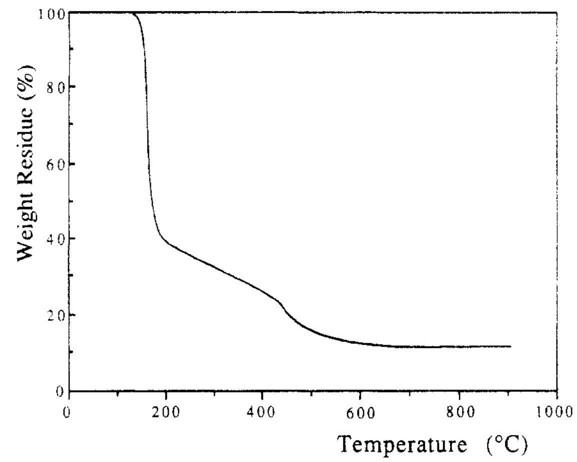


Figure 5. Thermogravimetric analysis of **3c** under nitrogen.

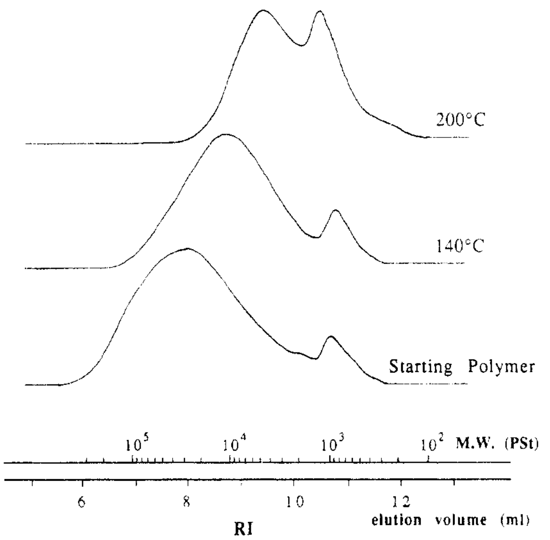


Figure 6. GPC traces for **3c** and the samples after heating at 140 °C and at 200 °C.

Experimental Section

Materials and Instruments. Chloroform was dried over phosphorus pentoxide and was distilled before use. Ethanol, benzene, and THF were used as received. **1** (existing as a dimer) was prepared as reported earlier[10] and was purified by distillation at 90–92 °C/0.1 mmHg (lit.[11] 98 °C/0.12 mmHg). **2a–f** were purified by distillation under reduced pressure. **2g** was recrystallized from ethyl acetate.

^1H NMR spectra were recorded in $CDCl_3$ on a Hitachi R-600 instrument (60 MHz, tetramethylsilane as an internal standard). ^{11}B NMR spectra were recorded in $CDCl_3$ on a JEOL JNM-JX-400 instrument (BF_3OEt_2 as an external standard). IR spectra were obtained on a Perkin-Elmer 1600 spectrometer. Gel permeation chromatographic analyses were carried out on a Tosoh HLC-8020 (TSK gel G4000) by using THF as an eluent after calibration with standard polystyrene samples. Thermogravimetric analysis (TGA) was made on a Shimadzu DT-30 instrument (15 °C/min) in air or in a nitrogen stream. Differential scanning calorimetry (DSC) was measured on a Seiko DSC-200 instrument (10 °C/min).

Hydroboration Polymerization of Dicyano Compounds (2a–g) with Di-*n*-butylborane (1). To a two-necked flask equipped with a magnetic stirrer bar, a septum inlet, and a three-way stopcock was added at room temperature under nitrogen, **2a** (0.032 g, 0.41 mmol), followed by **1** (0.120 g, 0.95 mmol). After 3 h at ambient temperature, the reaction product was dissolved in 2 mL of THF and precipitated into 30 mL of EtOH/H_2O (v/v, 1/1). The obtained polymer was freeze-dried with benzene. Yield: 0.119 g (88%). ^{1}H NMR (δ, ppm): 0.14–1.60 (*n*-Bu, 36H), 2.48 (N=CCH_2–, br m, 4H), 7.38 (N=CH–, br, 2H). IR (neat): 2954, 2917, 2870, 1684, 1459, 1376, 1222, 1098, 934, 798, 735 cm^{-1}.

In a similar manner, **3b–g** were obtained. **3b** was obtained from 0.047 g (0.50 mmol) of **2b** and 0.117 g (0.93 mmol) of **1**. Yield: 0.145 g (90%). ^{1}H NMR (δ, ppm): 0.14–1.94 (*n*-Bu, N=$CCCH_2$–, total 38H), 2.29 (N=CCH_2–, br m, 4H), 7.34 (N=CH–, br, 2H). IR (neat): 2917, 2868, 1682, 1464, 1376, 1220, 1097, 935, 807, 761 cm^{-1}. **3c** was obtained from 0.057 g (0.53 mmol) of **2c** and 0.119 g (0.95 mmol) of **1**. Yield: 0.133 g (78%), ^{1}H NMR (δ, ppm): 0.17–1.86 (*n*-Bu, N=$CCCH_2$–, total 40H), 2.27 (N=CCH_2–, br m, 4H), 7.34 (N=CH–, br, 2H). IR (neat): 2954, 2917, 2867, 1684, 1459, 1375, 1302, 1222, 1098, 1022, 935, 804, 733 cm^{-1}. **3d** was obtained from 0.069 g (0.57 mmol) of **2d** and 0.116 g (0.92 mmol) of **1**. Yield: 0.131 g (77%). ^{1}H NMR (δ, ppm): 0.14–1.75 (*n*-Bu, –CCH_2–, total 42H), 2.27 (N=CCH_2–, br m, 4H), 7.38 (N=CH–, br, 2H). IR (neat): 2954, 2917, 2869, 1684, 1452, 1376, 1304, 1223, 1097, 963, 933, 808, 772, 736 cm^{-1}. **3e** was obtained from 0.073 g (0.54 mmol) of **2b** and 0.118 g (0.94 mmol) of **1**. Yield: 0.138 g (76%). ^{1}H NMR (δ, ppm): 0.14–1.88 (*n*-Bu, –CCH_2–, total 44H), 2.52 (N=CCH_2–, br m, 4H), 7.38 (N=CH–, br, 2H). IR (neat): 2922, 2863, 1684, 1457, 1377, 1301, 1221, 1097, 1022, 939 cm^{-1}. **3f** was obtained from 0.086 g (0.53 mmol) of **2f** and 0.114 g (0.90 mmol) of **1**. Yield: 0.159 g (85%). ^{1}H NMR (δ, ppm): 0.10–1.87 (*n*-Bu, –CCH_2–, total 48H), 2.27 (N=CCH_2–, br m, 4H), 7.34 (N=CH–, br, 2H). IR (neat): 2921, 2860, 1684, 1458, 1376, 1301, 1221, 1097, 937, 808, 730 cm^{-1}. **3g** was obtained from 0.064 g (0.50 mmol) of **2g** and 0.119 g (0.95 mmol) of **1**. Yield: 0.049 g (25%). ^{1}H NMR (δ, ppm): 0.14–1.94 (*n*-Bu, 36H), 7.23–8.75 (N=CH–, C_6H_4, total 6H). IR (neat): 2954, 2917, 2868, 1701, 1649, 1438, 1373, 1228, 1156, 1097, 796, 690 cm^{-1}.

References and Notes

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