Polymer Bulletin 31, 553–558 (1993)

Polymer Bulletin

Hydroboration polymerization of dicyano compounds

III. Synthesis of poly(cyclodiborazane)s by the reaction of α,ω-dicyanoalkanes with thexylborane

Yoshiki Chujo*, Ikuyoshi Tomita[1], and Takeo Saegusa[2]

Division of Polymer Chemistry, Graduate School of Engineering, Kyoto University, Yoshida, Sakyo-ku, Kyoto 606-01, Japan

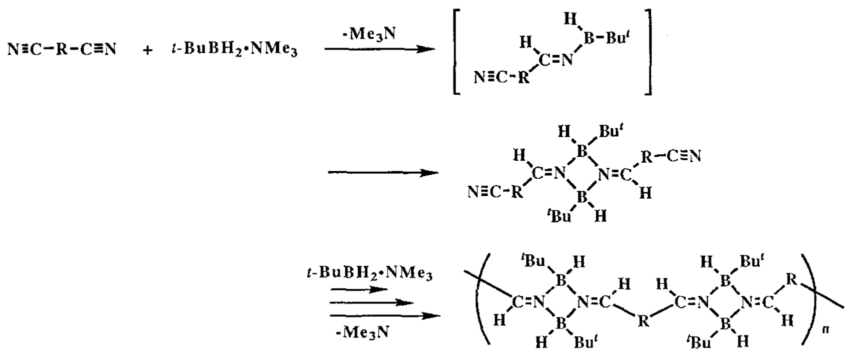
Summary

Hydroboration polymerization of various α,ω-dicyanoalkanes with thexylborane produced the corresponding poly(cyclodiborazane)s, that consist of boron-nitrogen four-membered rings. The structures of the obtained polymers were confirmed by spectroscopic analyses such as ^{1}H-, ^{11}B-NMR and IR spectra. From the result of thermogravimetric analysis of the polymer prepared from adiponitrile and thexylborane, 12% of the inorganic materials remained after heating at 900°C.

Introduction

We have recently explored novel methodologies for the preparation of boron-containing polymers consisting of boron-nitrogen four-membered rings (cyclodiborazane units). Hydroboration polymerization of dicyano compounds with t-BuBH$_2$•NMe$_3$ [3] or allylboration polymerization of dicyano compounds with triallylborane [4] 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 [5]. The poly(cyclodiborazane)s were found to be stable toward air and moisture in comparison with organoboron polymers prepared by hydroboration polymerization of dienes or diynes [6]. 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.

Scheme I



---

*Corresponding author

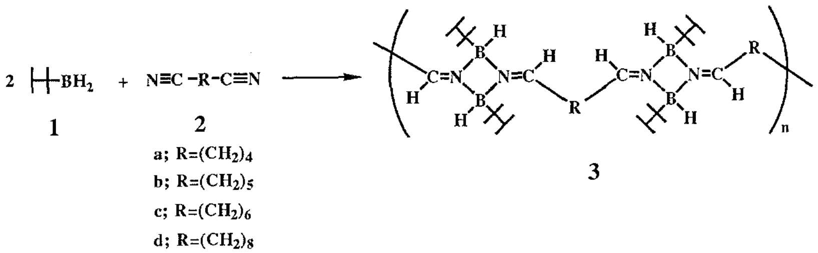
Footnotes 1 and 2, see references

In hydroboration polymerization of *t*-$BuBH_2•NMe_3$ [3], the iminoborane species is a key intermediate, which dimerizes to form cyclodiborazane units as shown in Scheme I. Aromatic dicyano compounds such as terephthalonitrile or isophthalonitrile gave the corresponding poly(cyclodiborazane)s effectively. However, in the cases of aliphatic dicyano compounds, the further hydroboration reaction of B-H species with iminoboranes causes the formation of only low molecular weight oligomers. This undesired side reaction was found to be influenced by the steric effect of the monoalkylborane used [7]. Here, we used thexylborane, which is more sterically hindered than *t*-$BuBH_2•NMe_3$, as a monomer in hydroboration polymerization of dicyano compounds, especially α,ω-dicyanoalkanes.

Results and Discussion

Thexylborane (**1**) is known to be stable in bulk without disproportionation [6]. **1** does not require the formation of complex with amine or sulfide for handling. However, the reaction of **1** with isophthalonitrile was very slow due to the steric hindrance of thexyl group, and no polymer was obtained under the conditions similar to that for hydroboration polymerization of isophthalonitrile with *t*-$BuBH_2•NMe_3$ [3]. Thus, α,ω-dicyanoalkanes (**2a**-**2d**) were used here for hydroboration polymerization with **1** (Scheme II). These aliphatic dicyano compounds are known to produce only low molecular weight oligomers by hydroboration with *t*-$BuBH_2•NMe_3$ due to side reactions.

Scheme II



As a typical example, hydroboration polymerization of adiponitrile (**2a**) with **1** was found to proceed smoothly without any solvent at room temperature. Within 1 hour, a colorless gum was produced and was isolated by reprecipitation from THF into ethanol/water (v/v=1/3). The obtained oligomer (**3a**) was soluble in common organic solvents such as THF or chloroform. Hydroboration polymerization of *t*-$BuBH_2•NMe_3$ required high reaction temperature (100°C) to provide free *t*-butylborane from its amine complex. In the case of **1**, however, the polymerization took place under much milder condition.

The structure of **3a** was elucidated by spectroscopic analyses such as ^{11}B-, ^{1}H-NMR, and IR spectra. In its ^{11}B-NMR spectrum (Figure 1), two major peaks at 33.7 and 3.2ppm were observed. The former peak can be attributed to the three coordinated boron species (i.e., monomeric iminoborane and/or dibora-amine species), and the latter to the dimeric iminoborane.

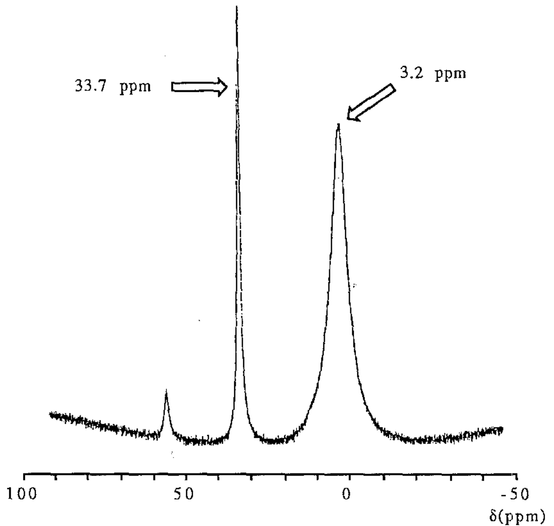


Figure 1. ^{11}B-NMR spectrum of poly(cyclodiborazane) (**3a**).

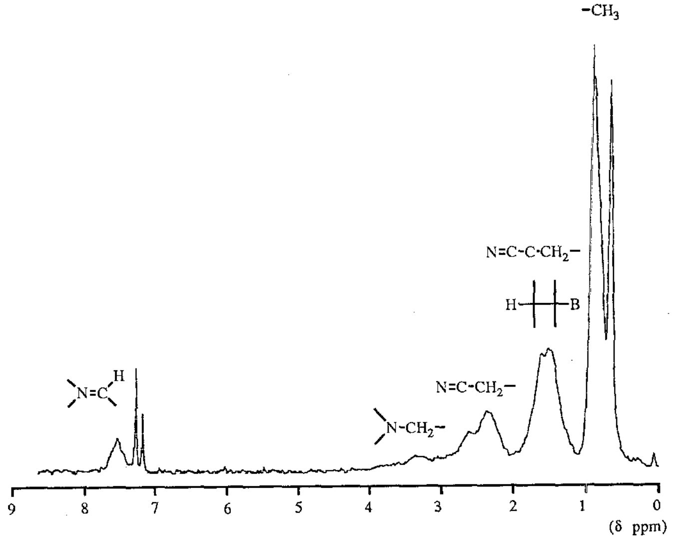


Figure 2. ^{1}H-NMR spectrum of poly(cyclodiborazane) (**3a**).

Figure 2 represents ^{1}H-NMR spectrum of **3a**. Methyl groups of thexyl moiety, inner methylenes, methylenes adjacent to iminoborane, and protons of imines were observed, respectively. The intensity of the peak for the protons of the imine was smaller than the expected in comparison with other peaks, and a small peak at 3.3ppm attributable to the methylenes adjacent to bora-amino group was observed. In IR spectrum of **3a** (Figure 3), specific stretching bands at 2,371 ($\upsilon_{B\text{-}H}$) and 1,673 cm^{-1} ($\upsilon_{C=N}$) were observed. No peaks attributable to nitrile nor monomeric iminoborane [8] were detected.

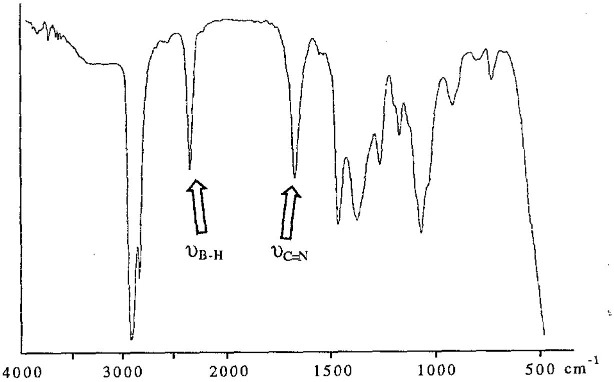


Figure 3. IR spectrum of poly(cyclodiborazane) (**3a**).

From these spectroscopic results, it can be concluded that the structure of the polymer obtained contains the expected cyclodiborazane backbones with a contamination of some dibora-amine species. In other words, the dimerization of iminoboranes takes place sufficiently. However, the low molecular weight of **3a** might be derived from some side reactions such as further hydroboration of iminoboranes with **1** to form the dibora-amines.

Table I. Hydroboration polymerization of various α,ω-dicyanoalkanes (2a-2d) with thexylborane (1).[a]

Run	α,ω-Dicyano-alkanes	Yield (%)[b]	$\overline{M}_n$[c]	$\overline{M}_w$[c]
1	$NC(CH_2)_4CN$ (2a)	54	1,250	3,680
2	$NC(CH_2)_5CN$ (2b)	48	1,030	3,520
3	$NC(CH_2)_6CN$ (2c)	63	740	1,660
4	$NC(CH_2)_8CN$ (2d)	58	660	1,460

a) Reactions were carried out in bulk at room temperature under nitrogen.
b) Isolated yields after reprecipitation into $EtOH/H_2O$ (v/v=1/3).
c) Estimated by GPC (polystyrene standards).

By using a similar procedure, hydroboration polymerization of several α,ω-dicyanoalkanes (**2b**-**2d**) with **1** was examined. These results are summarized in Table I. In all cases, the reactions were carried out in bulk, and the reaction mixture became viscous within 1 hour. All oligomers thus obtained (**3b**-**3d**) were confirmed to have cyclodiborazane backbones from the results of spectroscopic measurements. Though **1** has too sterically hindered alkyl substituents on the boron atom to attack the aromatic cyano groups, the higher steric hindrance in **1** in comparison with *t*-$BuBH_2•NMe_3$ made it possible to produce the oligomers from α,ω-dicyanoalkanes, that are difficult to be polymerized with *t*-$BuBH_2•NMe_3$ due to the dihydroboration reaction.

The oligomers (**3a**-**3d**) obtained by the present hydroboration polymerization were quite stable under air. From the result of thermogravimetric analysis of **3a** under nitrogen (Figure 4), it was found that 12% of the residue remained after heating at 900°C. This result indicates that the boron-containing oligomers prepared by hydroboration polymerization of α,ω-dicyanoalkanes with **1** can be expected as precursors for the boron-containing inorganic materials.

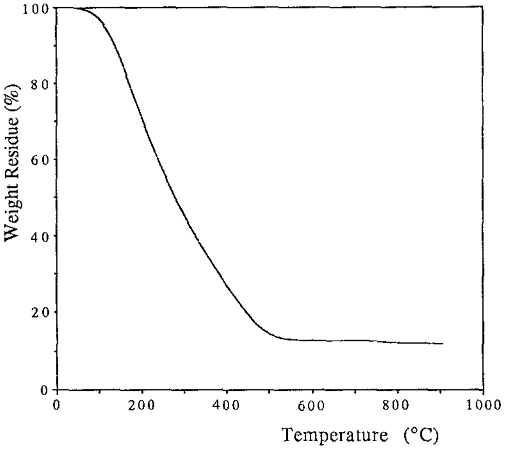


Figure 4. Thermogravimetric analysis of poly(cyclodiborazane) (**3a**) under nitrogen.

Experimental Section

Materials and Instruments. Thexylborane (**1**) was obtained by the reaction between borane-dimethyl sulfide and 2,3-dimethyl-2-butene as reported earlier [9], and was purified by distillation [6]. Isophthalonitrile was purified by recrystallization from ethyl acetate. α,ω-Dicyanoalkanes (**2a**-**2d**) were purified by distillation under reduced pressure.

^1H-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. ^{11}B-NMR spectrum was recorded in $CDCl_3$ on a JEOL JNM-JX-400 instrument (128MHz, BF_3OEt_2 as an external standard). Gel permeation chromatographic analyses were carried out on a Tosoh HLC-8020 (TSK Gel G3000) after calibration with standard polystyrene samples. Thermogravimetric analysis (TGA) was made on a Shimadzu DT-30 instrument (15°C/min.) under nitrogen stream.

Hydroboration Polymerization of α,ω-Dicyanoalkanes (2a-2d) with Thexylborane (1). A typical procedure is shown as follows (Table I, Run 1): To a nitrogen-replaced flask equipped with a stirrer tip and a three-way cock, **2a** (0.0657g, 0.608mmol) and then **1** (0.114g, 1.16mmol, 0.96 eq. for nitrile) were added at room temperature. In the early stage of the reaction, the reaction proceeded in two-phase system which turned to be a uniphase system as the reaction product became viscous (less than 30 min.). After reaction for 1 hour, the viscous reaction mixture was dissolved in THF and was precipitated into ethanol/water (v/v=1/3). After freeze-drying with benzene, **3a** was obtained as a colorless gum (0.100g, 54% yield). Spectral data are shown in the section of Results and Discussion.

Similarly, other boron-containing oligomers in Table I, Runs 2-4, were prepared from the corresponding α,ω-dicyanoalkanes (**2b**-**2d**) and **1**. **3b** prepared from **2b** (0.0685g, 0.561mmol) and **1** (0.114g, 1.16mmol): 48% yield (0.086g); ^{1}H-NMR (δ, ppm) 0.20-0.98 ($-CH_3$, m), 1.02-1.93 (CH, $-CH_2-C-C=N$, m), 1.93-2.78 ($-CH_2-C=N$, m), 3.28 ($-CH_2-N$, m), 7.59 (-CH=N, br, m), (integral ratios; 9.2:6.6:2.7:0.78:1); IR (neat) 2934, 2864, 2375, 1673, 1463, 1372, 1066, 932cm^{-1}. **3c** prepared from **2c** (0.0705g, 0.518mmol) and **1** (0.108g, 1.10mmol): 63% yield (0.108g); ^{1}H-NMR (δ, ppm) 0.22-1.05 ($-CH_3$, m), 1.08-2.00 (CH, $-CH_2-C-C=N$, m), 2.00-2.99 ($-CH_2-C=N$, m), 3.32 ($-CH_2-N$, m), 7.63 (-CH=N, br, m), (integral ratios; 16.9:14:6.1:2.1:1); IR (neat) 3316, 2930, 2862, 2371, 1672, 1465, 1403, 1266, 1065, 894, 759cm^{-1}. **3d** prepared from **2d** (0.0760g, 0.463mmol) and **1** (0.103g, 1.05mmol): 58% yield (0.097g); ^{1}H-NMR (δ, ppm) 0.37-1.04 ($-CH_3$, m), 1.07-1.90 (CH, $-CH_2-C-C=N$, m), 1.90-2.82 ($-CH_2-C=N$, m), 3.32 ($-CH_2-N$, m), 7.63 (-CH=N, br, m), (integral ratios; 15.4:17.4:5.9:1.8:1); IR (neat) 3206, 2928, 2859, 2370, 1672, 1464, 1371, 1065, 927, 757cm^{-1}.

References and Notes

1. Present address: Research Laboratory of Resources Utilization, Tokyo Institute of Technology, Nagatsuda, Midori-ku, Yokohama 227, Japan.
2. Present address: KRI International, 17 Chudoji, Minami-machi, Shimogyo-ku, Kyoto 600, Japan.
3. Chujo Y, Tomita I, Murata N, Mauermann H, Saegusa T (1992) *Macromolecules* 25: 27.
4. Chujo Y, Tomita I, Saegusa T (1992) *Macromolecules* 25: 3005.
5. Chujo Y, Tomita I, Asano T, Saegusa T (1993) *Polym. J.* 25: in press.
6. (a) Chujo Y, Tomita I, Hashiguchi Y, Tanigawa H, Ihara E, Saegusa T (1991) *Macromolecules* 24: 345. (b) Chujo Y, Tomita I, Hashiguchi Y, Saegusa T (1992) *Macromolecules* 25: 33. (c) Chujo Y, Tomita I, Saegusa T (1992) *Polym. Bull.* 27: 375.
7. Chujo Y, Tomita I, Saegusa T, the preceding paper in this issue.
8. Monomeric iminoboranes are known to have their C=N vibration spectra around 1,800 cm^{-1}. See, for example, (a) Mikhailov BM, Ter-Sarkisyan GS, Govorov NN, Nikolaeva NA (1976) *Izv. Akad. Nauk SSSR, Ser. Khim.* 1820. (b) Mikhailov BM, Ter-Sarkisyan GS, Govorov NN (1976) *Izv. Akad. Nauk SSSR, Ser. Khim.* 1823.
9. Brown HC, Mandal AK, Kulkarni SU (1977) *J. Org. Chem.* 42: 1392.

Accepted September 28, 1993 S