

Synthesis of Poly(cyclodiborazane)s by the Reaction of Bis(silylimine)s with Chlorodialkylboranes or with Methyl Dialkylborinates

Yoshiki CHUJO*, Ikuyoshi TOMITA**, Tsuyoshi ASANO,
and Takeo SAEGUSA***

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

(Received June 29, 1993)

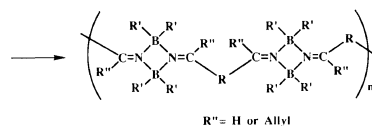
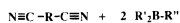
ABSTRACT: Poly(cyclodiborazane)s having boron-nitrogen four-membered structures in the main chains were prepared by the condensation reaction of bis(silylimine)s with substituted boranes such as chlorodialkylboranes and methyl dialkylborinates followed by cycloaddition of iminoborane species. Bis(silylimine)s prepared from terephthalaldehyde or isophthalaldehyde gave the corresponding polymers, whose number-average molecular weights (M_n) were around several thousands. The structures of poly(cyclodiborazane)s formed were confirmed by spectroscopic analyses such as ^1H , ^{11}B NMR, and IR spectra. The obtained polymers, however, became insoluble after exposure to air. On the other hand, when bis(silylimine)s derived from anthraquinone or sterically hindered boranes were used as a monomer, no polymerization took place.

KEY WORDS Boron-Containing Polymers / Poly(cyclodiborazane)s / Polycondensation / Bis(silylimine)s / Chlorodialkylboranes / Methyl Dialkylborinates /

We have explored novel methodologies for the preparation of organoboron polymers by means of haloboration polymerization¹ or hydroboration polymerization². The obtained polymers consist of carbon-boron bonds in their main chains and can be used as a novel type of versatile reactive polymers. Thus, poly(alcohol)s and poly(ketone)s were effectively prepared from these organoboron polymers.³

Recently, we also reported novel boron-containing polymers having boron-nitrogen four-membered rings (cyclodiborazane backbones) by hydroboration polymerization⁴ or allylboration polymerization⁵ of dicyano compounds (Scheme 1). The resulting poly(cyclo-

diborazane)s were found to be stable under air at room temperature. The boron-containing inorganic materials were obtained after pyrolysis of these poly(cyclodiborazane)s. In these systems, however, the substituents on boron atoms and on carbon atoms of imines were restricted for the preparation of high molecular weight polymers. As an alternative method for the preparation of poly(cyclodi-



R'' = H or Allyl

Scheme 1.

* To whom all correspondence should be addressed.

** Present address: *Research Laboratory of Resources Utilization, Tokyo Institute of Technology, Nagatsuda, Midori-ku, Yokohama 227, Japan.*

*** Present address: *KRI International, Chudoji, Shimogyo-ku, Kyoto 600, Japan.*

borazane)s, the condensation reactions can be used to generate the iminoborane species, which cyclize to form cyclodiborazane units. In these condensation reactions, a wide variety of polymer structures might be expected by changing the monomer structures.

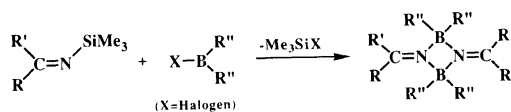
According to the previous report by Wade⁶, the reaction between *N*-silylimines and boron halides results mainly in the formation of iminoborane dimers, cyclodiborazanes (Scheme 2). This reaction is reported to proceed *via* the condensation between *N*-silylimine and boron halide, eliminating trimethylsilyl halide fol-

lowed by dimerization. In this reaction system, various substituents on boron atoms and on carbon atoms of imines could be used. Thus, the present paper describes a novel condensation method to prepare boron-containing polymers having cyclodiborazane backbones by the reaction using *N,N'*-bis(silylimine)s and substituted boranes (Scheme 3).

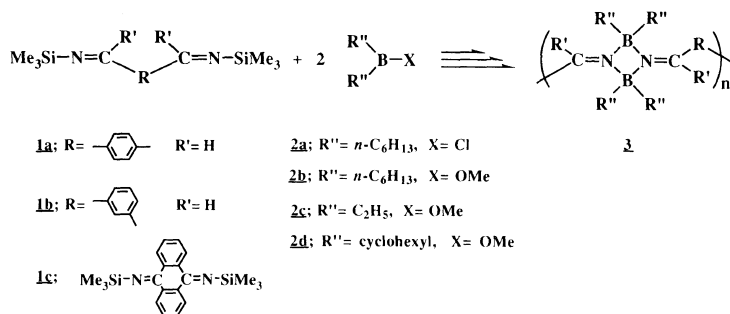
RESULTS AND DISCUSSION

Polycondensation between Bis(silylimine)s and Chlorodialkylboranes

The starting bis(silylimine)s (**1a**–**1c**) were prepared from the corresponding terephthalaldehyde, isophthalaldehyde or anthraquinone, respectively, according to the reported method.^{7,8} As a typical example of polycondensation, polymerization of *N,N'*-bis(tri-



Scheme 2.



Scheme 3.

Table I. Polymerization between **1a** and **2a** under various conditions

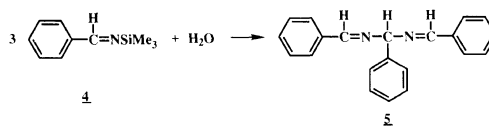
Run	2a/1a	Solvent ([M]) ^b	Reaction condition		\bar{M}_n^a	\bar{M}_w^a
1	2.03	Toluene (1)	r.t.	30 min	5000	7600
				1.5 h	4800	7200
2	2.12	CH ₂ Cl ₂ (1)	r.t.	30 min	4500	7100
				30 min	5800	9000
4	2.20	Toluene (1)	60°C	30 min	6000	10400
				2 h	6000	11500
				30 min	6000	10700
5	2.11	Toluene (1)	Reflux	15 min	6000	10700
				1 h	4000	5900
				2 h	3600	5100
6	2.19	Toluene (0.1)	r.t.	30 min	3600	4600

^a GPC measurement was performed without isolation.

^b Concentration of **1a**.

methylsilyl)terephthalaldehyde diimine (**1a**) with chlorodi(*n*-hexyl)borane (**2a**) was examined under various reaction conditions. The polymers obtained in the present study were subjected to GPC measurement without isolation. The results are summarized in Table I, from which the molecular weights of polymers (**3aa**) showed no significant change by the solvents used nor the reaction time (runs 1—3). At 60°C, however, the molecular weight of **3aa** was found to be slightly increased (run

4). At higher reaction temperature (run 5), or under much lower reaction concentration (run 6), the molecular weights of **3aa** slightly decreased. These results may show that the



Scheme 4.

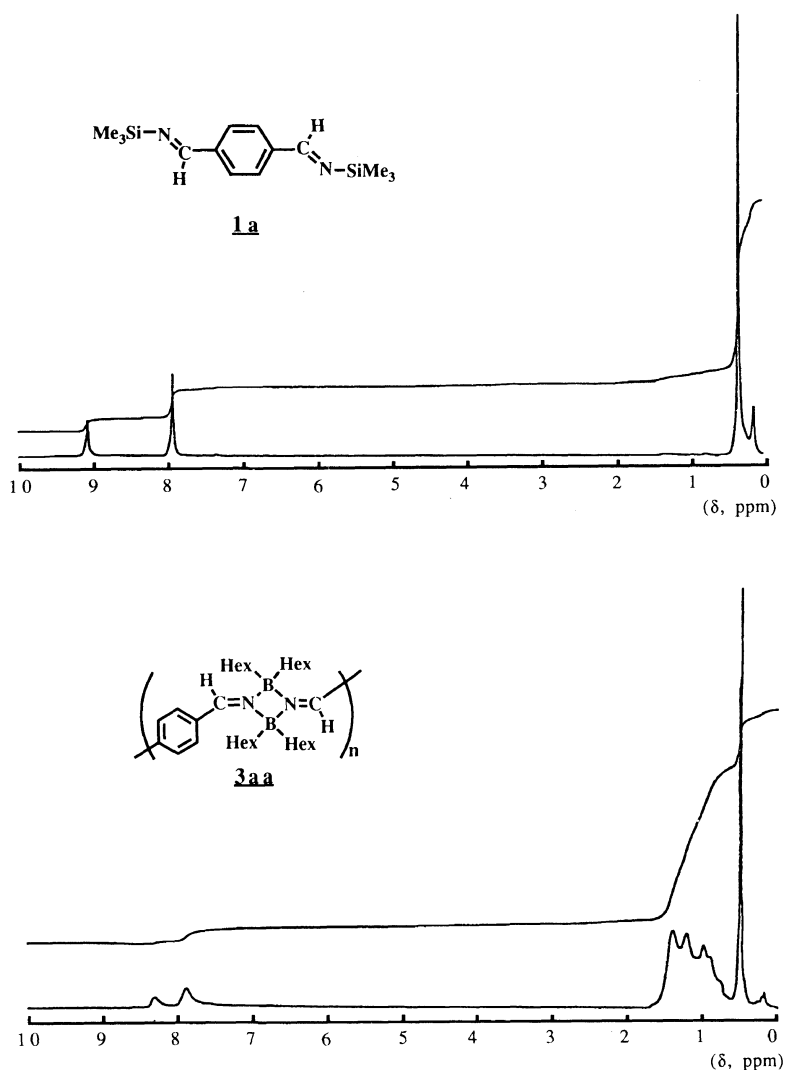


Figure 1. ^1H NMR spectra of bis(silylimine) (**1a**) and poly(cyclodiborazane) (**3aa**).

polymers obtained by this method were rather unstable at higher temperature as discussed in the previous papers concerning hydroboration polymerization⁴ or allylboration polymerization⁵ of dicyano compounds.

In order to isolate the polymer (**3aa**), the reaction mixture was precipitated into EtOH. The isolated polymer (**3aa**) was initially soluble in hot tetrahydrofuran (THF) or in hot CHCl₃. However, the isolated polymer became insoluble after keeping for several hours under air. The soluble part of the isolated polymer in hot THF was subjected to GPC measure-

ment. In comparison with GPC chart for the polymer before reprecipitation, the molecular weight of the isolated polymer increased.

According to the previous report, *N*-trimethylsilylbenzaldimine (**4**) is known to trimerize to form hydrobenzamide (**5**) via hydrolysis of *N*-trimethylsilyl group (Scheme 4).⁹ Therefore, if the conversion of *N*-silylimino groups to iminoborane species was not completed, the remained *N*-silylimino groups should be converted to imines by protonation. Imines thus generated are considered to trimerize to form hydrobenzamide derivatives. As a result, we may consider that, when the reaction mixture was reprecipitated into EtOH, these cross-linking reactions took place, and the molecular weights of the polymers were higher than those before reprecipitation.

Due to the instability of the polymer, the characterization of **3aa** was performed without reprecipitation. ¹H NMR spectra of the monomer **1a** and the polymer **3aa** are shown in Figure 1. After the polymerization reaction, the chemical shift of the proton on imino carbon was shifted from 9.04 ppm (*N*-silylimine) to 8.26 ppm (iminoborane). The integral ratios of the peaks attributable for **3aa** were in good agreement with the calculated values for the expected structure. In ¹¹B NMR of **3aa**, a broad peak around 6.2 ppm was observed, which was quite reasonable for the

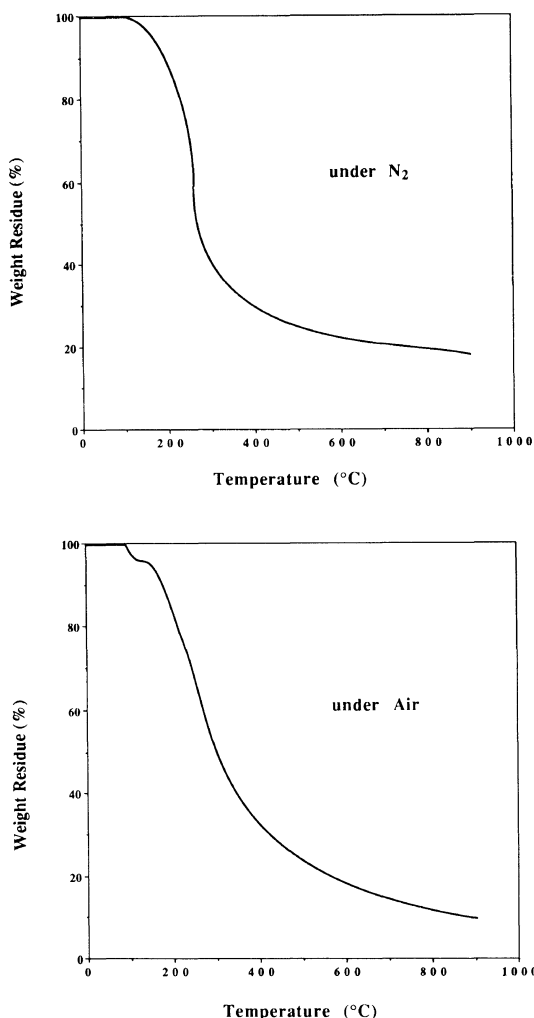


Figure 2. TGA curves of **3aa**.

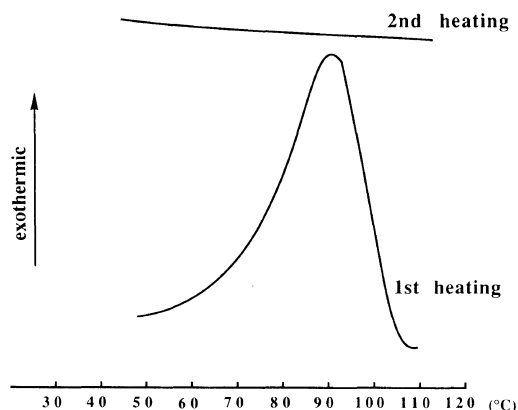


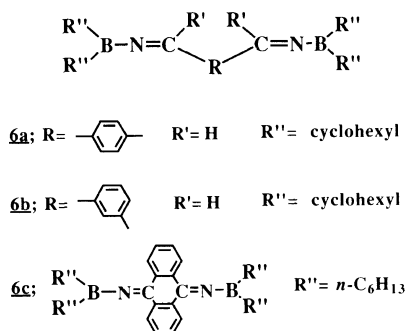
Figure 3. DSC curves of **3aa**.

four-coordinated boron-nitrogen species. In the IR spectrum, the peak assignable to the dimeric iminoborane species (1644 cm^{-1}) was observed.

Thermogravimetric analysis (TGA) of **3aa** was measured both under air and nitrogen (Figure 2). In both cases, a black solid (about 20 wt%) remained even after heating up to 900°C . This result indicates that poly(cyclodiborazane)s prepared by the present condensation polymerization can be expected as a precursor for boron-containing inorganic materials. The remained solid after pyrolysis of **3aa**, however, has not been characterized at present. Differential scanning calorimetry (DSC) was also measured under nitrogen (Figure 3), from which an irreversible exothermic peak was observed at the first scanning, but no peak at the second one. This may be due to some chemical reactions such as cross-linking taking place during heating.

Table II summarizes the results of polymerization reactions of **2a** using various bis(silylimine)s (**1a**–**1c**). Similarly to the case of **1a**, *N,N'*-bis(trimethylsilyl)isophthalaldehyde diimine (**1b**) gave the corresponding polymer (**3ba**), whose M_n and M_w were found to be 6300 and 9620, respectively, when 2.0 eq

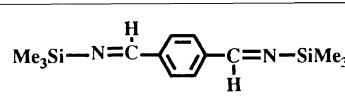
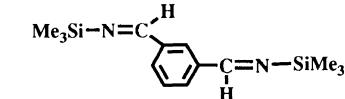
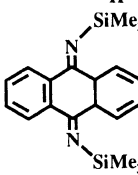
of **2a** was used. *N,N'*-Bis(trimethylsilyl)anthraquinone diimine (**1c**), however, gave no polymer, and only monomeric iminoborane (**6c**) was obtained. In IR spectrum of the reaction mixture, the stretching band of $\text{C}=\text{N}$ corresponding to monomeric iminoborane species (1776 cm^{-1}) was observed. That is, **1c** was converted to monomeric iminoborane species (**6c**), which, however, did not cyclize because of the steric-hindered structure.



Polycondensation between Bis(silylimine)s and Methyl Dialkylborinates

Poly(cyclodiborazane)s were found to be also prepared from **1a** and methyl dialkylborinates instead of **2a**. The results of polymerization reactions of two bis(silylimine)s

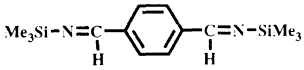
Table II. Polymerization between **2a** and **1a**–**1c**^a

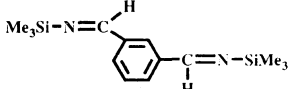
Run	<i>N,N'</i> -Bis(silylimine)		\bar{M}_n^b	\bar{M}_w^b
1		(1a)	5800	9000
2		(1b)	6300	9620
3		(1c)		no polymer

^a Polymerizations were carried out by adding small excess of **2a** to the 1M CDCl_3 solution of *N,N'*-bis(silylimine)s at 20°C .

^b GPC measurement was performed without isolation.

Table III. Polymerization between *N,N'*-bis(silylimine)s and various methyl dialkylborinates^a

Run	<i>N,N'</i> -Bis(silylimine)	Methyl dialkylborinate ^c	Product	Product	
				\bar{M}_n^b	\bar{M}_w^b
1	 (1a)	MeOB(Hex) ₂ (2b)	3ab	4260	6210
2 ^d		MeOB(Et) ₂ (2c)	3ac	9000	13900
3		MeOB(CHex) ₂ (2d)	6a	no polymer	

4	 (1b)	MeOB(Hex) ₂ (2b)	3bb	4400	6570
5 ^d		MeOB(Et) ₂ (2c)	3bc	3690	5300
6		MeOB(CHex) ₂ (2d)	6b	no polymer	

^a Polymerizations were carried out by adding small excess of methyl dialkylborinates to the 1M CDCl₃ solution of **1a** or **1b** at 20°C.

^b GPC measurement was performed without isolation.

^c Hex, *n*-hexyl group; Et, ethyl group; CHex, cyclohexyl group.

^d Reactions were carried out in THF.

(**1a** and **1b**) with various methyl dialkylborinates (**2b**, **2c**, and **2d**) are summarized in Table III. Similarly to **3aa**, the corresponding poly(cyclodiborazane)s (**3ab** and **3bb** from **2b**, **3ac** and **3bc** from **2c**) were obtained from methyl di(*n*-hexyl)borinate (**2b**) or from methyl diethylborinate (**2c**). The polymers (**3ac** and **3bc**, Table III, runs 2 and 5) were initially slightly soluble in hot THF or in hot CHCl₃, but became insoluble after several hours. In the case of methyl dicyclohexylborinate (**2d**), however, only monomeric iminoboranes (**6a** and **6b**, Table III, runs 3 and 6, respectively) were obtained from **1a** and **1b** due to the steric effect of cyclohexyl groups on boron atom.

In conclusion, poly(cyclodiborazane)s were prepared by the reaction of bis(silylimine)s with chlorodialkylboranes or with methyl dialkylborinates. This novel polymerization includes the condensation of two monomers followed by cycloaddition of iminoborane species formed. The present polymerization method may provide a useful synthetic way to prepare boron-containing polymers consisting of boron-nitrogen four-membered rings, *i.e.*, poly(cyclodiborazane)s.

EXPERIMENTAL

Materials and Instruments

Chlorodi(*n*-hexyl)borane (**2a**) was prepared by the reaction of monochloroborane-dimethyl sulfide complex and 1-hexene, as reported earlier¹⁰, and was purified by distillation (90–94°C/1 mmHg). Methyl di(*n*-hexyl)borinate (**2b**) was prepared by treatment of **2a** with methanol and was purified by distillation (75–76°C/1 mmHg). Methyl diethylborinate (**2c**) was prepared by methanolysis of the readily available triethylborane using pivalic acid as a catalyst¹¹ and was purified by distillation (45°C at normal pressure). Tetrahydrofuran and diethyl ether were dried over lithium aluminum hydride and were distilled before use. Benzene, diglyme, and toluene were dried over sodium and were distilled before use. CDCl₃ was dried over molecular sieves 4A. Dichloromethane was dried over P₂O₅ and distilled before use. 1,1,1,3,3,3-Hexamethyldisilazane and chlorotrimethylsilane were purified by distillation. *n*-Butyllithium (*n*-hexane solution) was obtained from Nakalai Tesque Inc., and was titrated before use.

¹H NMR spectra were recorded in CDCl₃

on a Hitachi R-600 instrument. ^{11}B NMR spectra were recorded in CDCl_3 on a JEOL JNM-JX-400 instrument. IR spectra were obtained on a Perkin Elmer 1600 spectrometer. Gel permeation chromatographic analyses were carried out on a Tosoh HLC-8020 (TSK gel G3000, or G4000) by using THF as an eluent after calibration with standard polystyrene samples. Thermogravimetric analysis (TGA) was made on a Shimadzu DT-30 instrument ($15^\circ\text{C min}^{-1}$) under air or nitrogen stream. Differential scanning calorimetry (DSC) was measured on a Seiko DSC200 instrument ($10^\circ\text{C min}^{-1}$) under nitrogen.

Preparation of $\text{LiN}(\text{SiMe}_3)_2$ ⁹

To a diethyl ether solution of $\text{HN}(\text{SiMe}_3)_2$, an *n*-hexane solution of *n*-butyllithium was added slowly under nitrogen. After refluxing for 30 min, a white solid precipitated, and then, the solvent was distilled off. The resulting product was used without further purification.

Preparation of Bis(silylimine)s^{7,8}

To a 30 ml benzene solution of $\text{LiN}(\text{SiMe}_3)_2$ (prepared from 3.87 g, 24 mmol of $\text{HN}(\text{SiMe}_3)_2$ and 14.2 ml, 20 mmol of 1.41 *N* *n*-butyllithium in *n*-hexane) was added terephthalaldehyde (1.33 g, 10 mmol) in 25 ml benzene dropwise at 50°C under nitrogen. After stirring for 3 h at 70°C , chlorotrimethylsilane (2.17 g, 20 mmol) in 10 ml benzene was added to the reaction mixture and this mixture was refluxed for 3 h. The resulting mixture was cooled and then filtered to remove lithium chloride. After evaporation of the solvent, Kugelrohr distillation ($130^\circ\text{C}/1\text{ mmHg}$) gave 1.68 g (6.1 mmol, 61% yield) of **1a**. **1a**: ^1H NMR (δ , CDCl_3) 0.27 ($-\text{SiMe}_3$, s, 18H), 7.89 (C_6H_4 , s, 4H), and 9.06 ($-\text{CH}=\text{N}-$, s, 2H); IR (cell, CDCl_3) 3023, 2961, 1642, 1423, 1216, 1095, 1023, and 852 cm^{-1} ; mp $75-82^\circ\text{C}$.

In a similar manner, **1b** was obtained in 61% ($130^\circ\text{C}/0.85\text{ mmHg}$). **1b**: ^1H NMR (δ , CDCl_3) 0.27 ($-\text{SiMe}_3$, s, 18H), 7.73–8.32 (C_6H_4 , 4H), and 9.08 ($-\text{CH}=\text{N}-$, s, 2H); IR (cell, CDCl_3)

2960, 2827, 1648, 1432, 1254, 1142, 1079, and 852 cm^{-1} ; mp $45-48^\circ\text{C}$.

To a 50 ml benzene suspension of anthraquinone (1.98 g, 9.5 mmol), 26 ml of a benzene solution of $\text{LiN}(\text{SiMe}_3)_2$ (prepared from 5.65 g, 35 mmol of $\text{HN}(\text{SiMe}_3)_2$ and 20 ml, 28.2 mmol of 1.41 *N* *n*-butyllithium in *n*-hexane) was added slowly by a dropping funnel at 70°C under nitrogen. After refluxing for 6 h, chlorotrimethylsilane (3.06 g, 28.2 mmol) in 10 ml benzene was added slowly at that temperature. The reaction mixture was refluxed for 4 h, and then cooled. This mixture was filtered to remove lithium chloride. After evaporation of the solvent, Kugelrohr distillation ($150^\circ\text{C}/0.5\text{ mmHg}$) gave 1.39 g (4.0 mmol, 42% yield) of **1c**. **1c**: ^1H NMR (δ , CDCl_3) 0.45 ($-\text{SiMe}_3$, s, 18H), and 7.16–8.38 (aromatic, 8H); IR (cell, CDCl_3) 2957, 1673, 1255, 1031, 938, and 845 cm^{-1} ; mp $100-110^\circ\text{C}$ (lit.¹⁰ $118-120^\circ\text{C}$).

Polycondensation between Bis(silylimine)s and Chlorodialkylboranes

A typical example is as follows. To a 1M CDCl_3 solution of **1a** (0.27 g, 0.98 mmol) was added **2a** (0.44 g, 2.0 mmol) slowly by using a syringe at room temperature under nitrogen. After 30 min stirring at that temperature, the reaction mixture was subjected directly to GPC analysis. The spectroscopic data of the obtained polymer (**3aa**) are given in the text. In a similar manner, **3aa** was prepared under various conditions. These results are summarized in Table I. The same structure of **3aa** was also prepared from **1a** (0.14 g, 0.49 mmol) and **2b** (0.22 g, 1.0 mmol) by using a similar procedure (**3ab**, Table III, run 1).

Poly(cyclodiborazane) (**3ba**) was similarly prepared from **1b** (0.17 g, 0.6 mmol) and **2a** (0.25 g, 1.2 mmol) as for **3aa**. **3ba**: ^1H NMR (δ , CDCl_3) 0.49–1.62 (hexyl, 52H), 7.38–8.04 (C_6H_4 , 4H), and 8.26 ($-\text{CH}=\text{N}-$, s, 2H); IR (cell, CDCl_3) 2923, 2857, 1646, 1461, 1255, 1081, and 848 cm^{-1} . **3bb** (the same structure as **3ba**) was also prepared from **1b** (0.22 g,

0.8 mmol) and **2b** (0.34 g, 1.62 mmol) in a similar manner (Table III, run 4).

The monomeric iminoborane (**6c**) was obtained from **1c** (0.32 g, 0.9 mmol) and **2a** (0.39 g, 1.8 mmol). **6c**: $^1\text{H NMR}$ (δ , CDCl_3) 7.45–8.09 (aromatic, 8H), and 0.43–1.61 (hexyl, 52H); IR (cell, CDCl_3) 2922, 2860, 1776, 1458, 1295, 1056, and 848 cm^{-1} .

Polycondensation between Bis(silylimine)s and Methyl Dialkylborinates

Similarly to **3aa**, poly(cyclodiborazane)s (**3ac** and **3bc**) and monomeric iminoboranes (**6a** and **6b**) were prepared as follows. **3ac**: from **1a** (0.21 g, 0.76 mmol) and **2c** (0.16 g, 1.6 mmol); $^1\text{H NMR}$ (δ , CDCl_3) 0.88 (ethyl, 20H), 7.83 (C_6H_4 , 4H), 8.26 ($-\text{CH}=\text{N}-$, s, 2H); IR (cell, CDCl_3) 2925, 2862, 1642, 1460, 1376, 1266, 1052, and 846 cm^{-1} . **3bc**: from **1b** (0.22 g, 0.8 mmol) and **2c** (0.16 g, 1.6 mmol); $^1\text{H NMR}$ (δ , CDCl_3) 0.86 (ethyl, 20H), 7.50–7.98 (C_6H_4 , 4H), and 8.28 ($-\text{CH}=\text{N}-$, s, 2H); IR (cell, CDCl_3) 2950, 2874, 1647, 1461, 1344, 1254, 1073, and 844 cm^{-1} . **6a**: from **1a** (0.28 g, 1.0 mmol) and **2d** (0.46 g, 2.2 mmol); $^1\text{H NMR}$ (δ , CDCl_3) 0.75–2.05 (cyclohexyl, 48H), 7.86 (C_6H_4 , 4H), and 8.26 ($-\text{CH}=\text{N}-$, s, 2H); IR (cell, CDCl_3) 2921, 2847, 1803, 1643, 1447, 1372, 1255, 1081, and 850 cm^{-1} . **6b**: from **1b** (0.22 g, 0.8 mmol) and **2d** (0.34 g, 1.6 mmol); $^1\text{H NMR}$ (δ , CDCl_3) 0.76–2.03 (cyclohexyl, 48H), 7.32–7.83 (C_6H_4 , 4H), and 8.26 ($-\text{CH}=\text{N}-$, s, 2H); IR (cell, CDCl_3) 2919, 2847,

1807, 1644, 1447, 1322, 1256, 1080, and 845 cm^{-1} .

REFERENCES

1. Y. Chujo, I. Tomita, and T. Saegusa, *Macromolecules*, **23**, 687 (1990).
2. a) Y. Chujo, I. Tomita, Y. Hashiguchi, H. Tanigawa, E. Ihara, and T. Saegusa, *Macromolecules*, **24**, 345 (1991). b) Y. Chujo, I. Tomita, Y. Hashiguchi, and T. Saegusa, *Macromolecules*, **25**, 33 (1992). c) Y. Chujo, I. Tomita, and T. Saegusa, *Polym. Bull.*, **27**, 375 (1992).
3. a) Y. Chujo, I. Tomita, Y. Hashiguchi, and T. Saegusa, *Macromolecules*, **24**, 3010 (1991). b) Y. Chujo, I. Tomita, Y. Hashiguchi, and T. Saegusa, *Polym. Bull.*, **25**, 1 (1991). c) Y. Chujo, I. Tomita, and T. Saegusa, *Polym. Bull.*, **26**, 165 (1991). d) Y. Chujo, M. Morimoto, and I. Tomita, *Polym. Bull.*, **29**, 617 (1992). e) Y. Chujo, M. Morimoto, and I. Tomita, *Polym. J.*, **25**, 891 (1993).
4. Y. Chujo, I. Tomita, N. Murata, H. Mauermann, and T. Saegusa, *Macromolecules*, **25**, 27 (1992).
5. Y. Chujo, I. Tomita, and T. Saegusa, *Macromolecules*, **25**, 3005 (1992).
6. a) C. Summerford and K. Wade, *J. Chem. Soc. (A)*, 1487 (1969). b) C. Summerford and K. Wade, *J. Chem. Soc. (A)*, 2010 (1970).
7. C. Krueger, E. G. Rochow, and U. Wannagat, *Chem. Ber.*, **96**, 2132 (1963).
8. L. Chan and E. G. Rochow, *J. Organometal. Chem.*, **9**, 231 (1976).
9. E. H. Amonoo-Neizer, R. A. Shaw, D. O. Skovlin, and B. C. Smith, *J. Chem. Soc.*, 2997 (1965).
10. H. C. Brown, N. Ravindran, and U. Kulkarni, *J. Org. Chem.*, **44**, 2417 (1979).
11. R. Koester, K. Amew, W. Bellut, and W. Fenzyl, *Angew. Chem. Int. Ed.*, **10**, 748 (1971).