Hydroboration Polymerization of Dicyano Compounds. 1. Synthesis of Boron-Containing Polymers by the Reaction between t-BuBH$_2$·NMe$_3$ and Dicyano Compounds

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ABSTRACT: A new methodology for the preparation of air-stable boron-containing polymers by the polyaddition between dicyano compounds and t-BuBH$_2$·NMe$_3$ (1) is described. The polyaddition between 1 and isophthalonitrile (**2a**) was carried out in diglyme under some varied conditions. The molecular weight of the resulting polymer (**3a**), estimated by GPC, increased when a small excess amount of 1 was used for this polymerization. The structure of **3a** was confirmed by ^{1}H, ^{13}C, and ^{11}B NMR, UV, and IR analyses. The stability of **3a** against air and moisture as well as its thermal stability was examined. The boron-containing polymer **3a** was found to be stable under air and moisture. As dicyano compounds, telephthalonitrile (**2b**), 1,5-bis(4,4′-cyanophenoxy)pentane (**2c**), and α,ω-dicyanoalkanes (**2d–f**) were also used in the present hydroboration polymerization. Among these compounds, the monomers having aromatic cyano groups gave polymers with higher molecular weights.

Introduction

Recently, we have reported the sythesis of novel organoboron polymers. For example, polyaddition between dienes and thexylborane by means of hydroboration gave the corresponding organoboron polymers,[1] which were proven to have the interesting characteristics as novel reactive polymers to produce poly(alcohol)s or poly(ketone)s.[2] Poly(organoboron halide)s formed by the polyaddition between boron tribromide and terminal diynes were also reported to have novel reactivities as a poly(Lewis acid).[3]

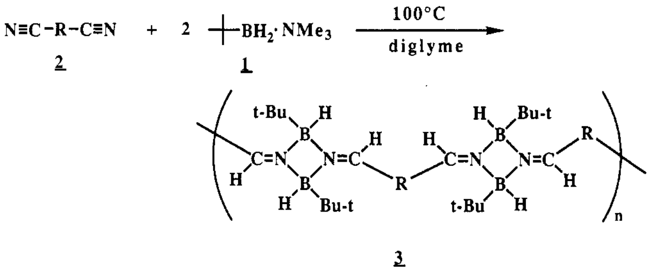
On the other hand, the preparation of stable boron-containing polymers has been an attractive target because a few examples such as borazine, phosphinoborane, and decarborane polymers[4] have been reported as the polymeric materials or as the precursors of inorganic materials[5] after pyrolysis. Here, we wish to present a novel method for obtaining air-stable boron-containing polymers by the polyaddition between dicyano compounds and *tert*-butylborane–trimethylamine (1) (Scheme I). The resulting boron-containing polymers having cyclodiborazane backbones (i.e., boron–nitrogen four-membered rings) were found to be stable enough under air and moisture.

Results and Discussion

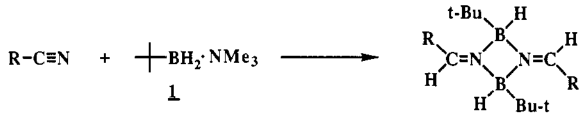
According to a previous report by Hawthorne,[6] the reaction between 1 and various nitrile compounds results mainly in the formation of iminoborane dimers, i.e., cyclodiborazanes (Scheme II). The formation of these boron–nitrogen four-membered rings was reported also in the cases of the reactions between allylboranes and nitriles,[7] thioesters of dialkylboronic acids and imines,[8] tetraalkyldiborane and nitrile,[9] and so on.[10] These compounds were reported to be stable enough against air and moisture. This fact prompted us to build up a boron-containing polymer with this structure. First, polyaddition by using the reaction reported by Hawthorne[6] was examined with bifunctional dicyano compounds.

Hydroboration Polymerization between 1 and Isophthalonitrile (2a). As a preliminary example, polymerization of **2a** and 1 was examined to optimize the reaction conditions. All the reactions were carried out in a diglyme solution under nitrogen atmosphere. The molecular weights of the resulting polymers were estimated by GPC (THF as an eluent) after calibration with standard polystyrenes although the structures between them were somewhat different. The results are summarized in Table I. In runs 1, 2, and 5, the effect of reaction temperature was examined. From these results, polymerization at 100 °C was shown to be the best condition. In order to obtain the moderate reactivity from 1, it is necessary to remove the trimethylamine ligand by means of heating. At 120 °C, however, the resulting polymer seemed to contain another structure,[11] possibly due to the undesirable side reaction. As a result, when the reaction was carried out at 140 °C, gelation was observed. The reaction time was varied at 100 °C (runs 2–4), from which the decomposition of the polymer was observed after longer heating (vide infra). When the reaction mixture (run 2) was precipitated into EtOH/H$_2$O (v/v = 1/1), a white solid was obtained in a 96% yield. The obtained polymer (**3a**) was soluble in various organic solvents such as THF, CH$_2$Cl$_2$, CHCl$_3$, and benzene.

Scheme I



Scheme II



The dependence of molecular weight on the feed ratio between the two monomers (1/**2a**) was examined. As is shown in Table II and Figure 1, by increasing the feed ratio of 1/**2a**, the molecular weight of the resulting polymer

Table I
Polymerization Conditions between 1 and 2a[a]

run	[t-BuBH$_2$·NMe$_3$]/ [C≡N] ratio	reaction conditions	$\bar{M}_n$[b]	$\bar{M}_w$[b]	yield[c] (%)
1	1.02	80 °C, 1 h	1240	1990	–
2	0.99	100 °C, 1 h	4030	6140	96
3	1.05	100 °C, 2 h	1320	2170	–
4		4.5 h	550	690	–
5	0.98	120 °C, 1 h	3680	12600	93

[a] Reactions were carried out in diglyme. [b] GPC, polystyrene standard. [c] Isolated yield after precipitation into EtOH/H$_2$O (v/v = 1/1).

Table II
Effect of Feed Ratio of 1/2a[a]

run	[t-BuBH$_2$·NMe$_3$]/ [C≡N] ratio	$\bar{M}_n$[b]	$\bar{M}_w$[b]	yield[c] (%)
1	0.32	500	680	–
2	0.49	870	1250	–
3	0.82	1630	3320	–
4	0.99	4030	6140	96
5	1.55	7590	27200	96
6	2.17	6610	26000	96
7	2.97	7080	30300	98

[a] Reactions were carried out in diglyme. [b] GPC, polystyrene standard. [c] Isolated yield after precipitation into EtOH/H$_2$O (v/v = 1/1).

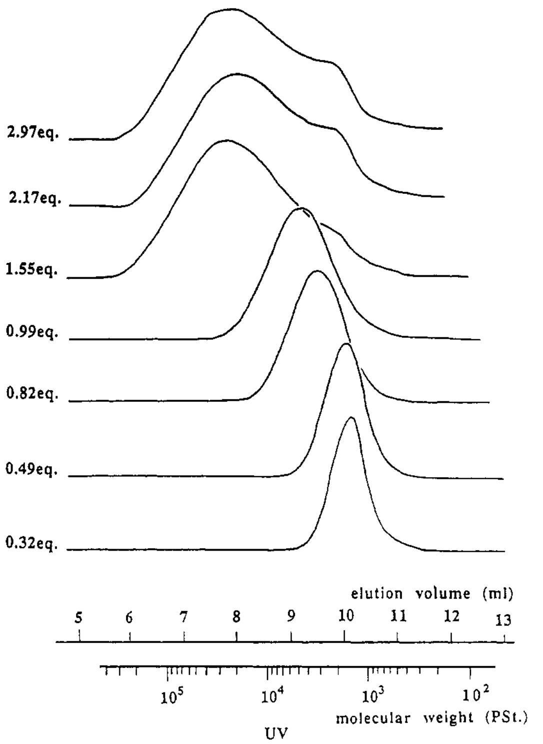
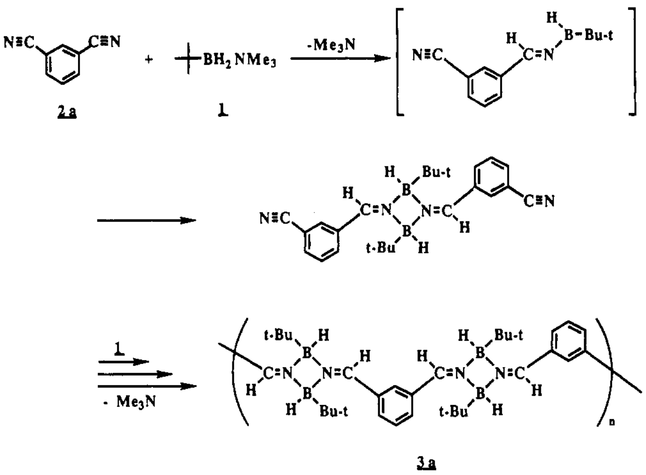


Figure 1. Dependence of molecular weight of **3a** on the feed ratio of the monomer **1**/**2a**.

increased. It was found that the polymerization with a small excess amount of **1** gave a polymer having a higher molecular weight than that with a stoichiometric amount of **1** (run 4 vs 5). However, a further excess amount of **1** had no more effect on the molecular weight (runs 6, 7).

Polymerization should proceed as illustrated in Scheme III. Accordingly, the formation of an iminoborane species should be essential for this polymerization. On the assumption that the iminoborane species never reacts further with an excess of **1**, the higher conversion of the nitrile group into iminoborane should be favorable for this polymerization, which is considered to be achieved by using a small excess amount of **1**. This assumption was confirmed by a model reaction between **1** and benzonitrile (**4**) as well as by the comparison of spectroscopic data of obtained polymers from varying the feed ratio of **1**/**2a** (vide infra). The conversion curve of **4** followed by GC analysis is shown in Figure 2. It is seen that a small excess amount of **1** brings about a quantitative conversion of **4**. When a 2-fold excess of **1** was reacted with **4**, the aiming product (**5**) was isolated in the yield of 90%.[12] This finding is used to rationalize the improved result of polymerization with an excess amount of **1**.

Scheme III



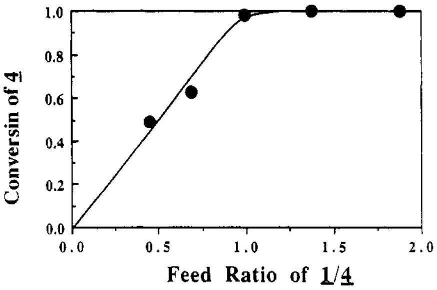
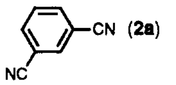
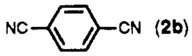
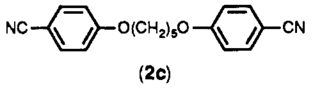


Figure 2. GC conversion curve of **4** by the reaction with **1**.

Table III
Synthesis of Boron-Containing Polymers from Various Dicyano Compounds and 1[a]

run	dicyano compound	[t-BuBH$_2$·NMe$_3$]/ [C≡N] ratio	$\bar{M}_n$[b]	$\bar{M}_w$[b]	yield[c] (%)
1	 (**2a**)	1.55	7590	27200	96
2	 (**2b**)	1.94	3280	12000	84
3	 (**2c**)	1.73	6440	21400	93
4[d]	NC(CH$_2$)$_4$CN (**2d**)	0.89	810	1380	–
5[d]		1.65	300	400	–
6[d]	NC(CH$_2$)$_6$CN (**2e**)	0.93	780	990	–
7[d]	NC(CH$_2$)$_8$CN (**2f**)	1.03	750	1710	–

[a] Reactions were carried out at 100 °C for 1 h in diglyme. [b] GPC, polystyrene standard. [c] Isolated yield after precipitation into EtOH/H$_2$O (v/v = 1/1). [d] GPC was measured without isolation.

Hydroboration Polymerization of Various Dicyano Compounds. The present hydroboration polymerization was also examined using various dicyano compounds. The results are summarized in Table III. Instead of **2a**, terephthalonitrile (**2b**) and 1,5-bis(4,4′-cyanophenoxy)pentane (**2c**) also gave the corresponding polymers

Table IV
IR Data of the Boron-Containing Polymer 3a Prepared under Various Conditions

	IR (cm^{-1})			
sample	2366 (ν_{B-H})	2239 ($\nu_{C\equiv N}$)	1645 ($\nu_{C=N}$)	1479 ($\nu_{C=C}$)
Table II, run 3	0.98	0.26	1.52	1
Table II, run 4	1.11	0.11	1.63	1
Table II, run 5	1.08	0	1.82	1
Table II, run 7	1.17	0	1.83	1
Table I, run 5	0.82	0.05	1.59	1

(**3b**, **3c**, respectively) whose M_n was found to be 3280 and 6440, respectively, when small excess of **1** was used. Aliphatic dicyano compounds (**2d–f**), however, resulted in the formation of oligomers with very low molecular weights. IR and ^{1}H NMR spectra of **3d–f** (from aliphatic dicyano monomers) indicate that the further hydroboration reaction of the iminoborane species did take place during the polymerization. By the Rimini test of the obtained oligomers, the presence of a primary amine was also detected. This side reaction produced a diboraamine species, which should be readily cleaved during the measurement of the GPC. This is taken to be one of the reasons for the poor results with aliphatic dicyano compounds.

Characterization of Boron-Containing Polymers. Structure elucidation of **3a** was performed by comparison with spectroscopic data of model compound (**5**)[6] in ^{1}H, ^{13}C, and ^{11}B NMR, UV, and IR spectra. In the IR spectrum of **3a**, the peaks due to B—H stretching (2350–2400 cm^{-1}), and C═N stretching (1645 cm^{-1}) were observed to be similar to those of **5**. The intensities of the peaks for B—H, C≡N, and C═N of the boron-containing polymers prepared with some varied feeding ratios of **1**/**2a** are calculated relative to the peak at 1479 cm^{-1} (Table IV). From these results, no decrease of C═N nor increase of B—H was observed even in the polymer prepared with 3 equiv of **1**. Thus, this result is taken to mean that the iminoborane species is less reactive toward further hydroboration reaction. On the other hand, the disappearance of the peak for C≡N was observed when excess **1** was used. As mentioned above, these results indicate that an excess of **1** only reacts with C≡N, which brings about higher molecular weight polymers with the expected structure.

In the ^{11}B NMR spectra of **3a** and **3c**, a single broad peak around −1.7 and 5.1 ppm, respectively, was observed, which was close to the corresponding chemical shift for the model compound (**5**) (5.7 ppm).[13] In addition, these values are quite reasonable for the four-coordinated boron species. In the UV spectrum, **3a** showed an absorption maxima at 259 nm, while **5** had an absorption maxima at 273 nm (ϵ = 11 400).[6] The lower wavelength peak in the polymer can be ascribed to the torsion of the plane of the aromatic ring and the conjugated C═N bonds caused by the doubly attached *tert*-butyl groups which is only effective for one *tert*-butyl group per aromatic group in the structure of **5**. In fact, **3c** showed an absorption maxima at 302 nm (in CH_2Cl_2), which was the same for the model compound **6** (302 nm, ϵ = 18 000).[6] By using a molar absorptivity of **6**, the boron–nitrogen four-membered structure in **3c** was detected quantitatively (98% for the expected). In their ^{1}H NMR spectra, as shown in Figure 3, both **3a** and **5** showed peaks assignable to the protons of imine, benzene ring, and *tert*-butyl groups. The integral ratios of these peaks for **3a** were in good agreement with the calculated values for the expected structure.

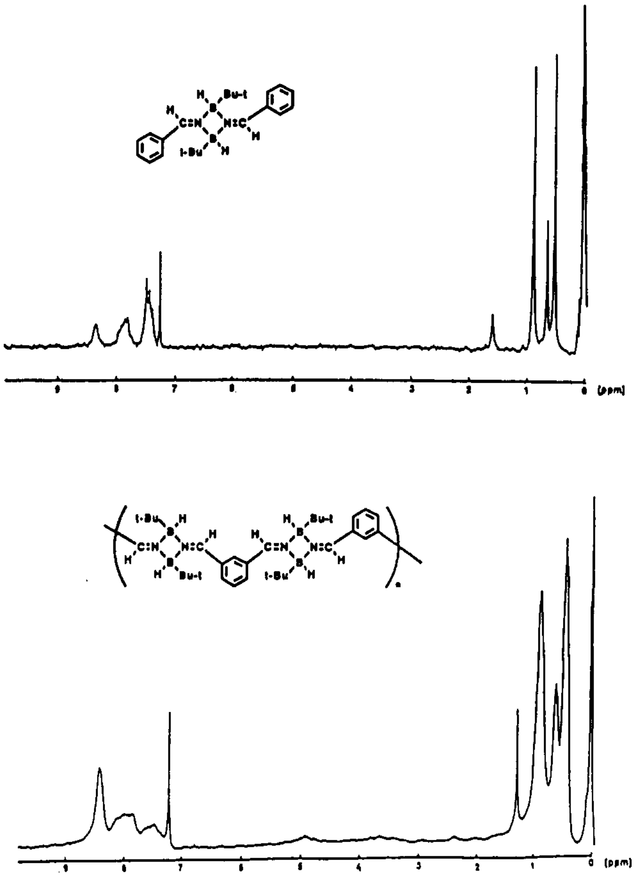
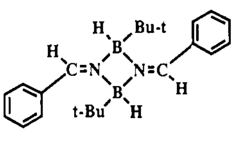
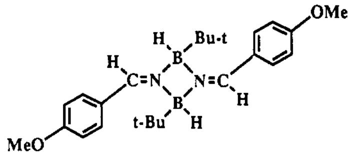


Figure 3. ^{1}H NMR spectra of the boron-containing polymer **3a** and model compound **5**.



5



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In the ^{13}C NMR spectrum of **3a**, a peak around 156.6 ppm assignable to the imino carbon was observed, while any peaks due to nitrile (120 ppm) and amine (46 ppm) were not detected (Figure 4). Resonances of *tert*-butyl groups in **3a** were quite similar to the corresponding peaks of **5** (Figure 4). The multiplicity of these peaks was possibly due to the four possible configurations of four-membered structure (i.e., cis-syn, trans-syn, cis-anti, and trans-anti isomeric structures).

According to the previous description,[6] the formation of a six-membered ring is not negligible. Thus, the possibility of the contamination of this structure (i.e., branched structure) in the resulting polymer in the present study should not be eliminated (Scheme IV). At least, however, gelation was never observed during the polymerization at 100 °C in the present study.

Stability of 3a against Moisture and Air. The stability of **3a** against air was demonstrated by monitoring the change of molecular weight in the GPC while air was bubbled (120 mL/min) into a chloroform solution of **3a** for 1 h. The stability of **3a** against moisture was similarly checked by stirring the chloroform solution of **3a** with water for 2 days under nitrogen. In both cases, no obvious change in its molecular weight was observed on comparison with that of the starting polymer (Figure 5). ^{1}H NMR and IR spectra of the polymer either after air bubbling or after water shaking study were identical to those of the starting polymer.

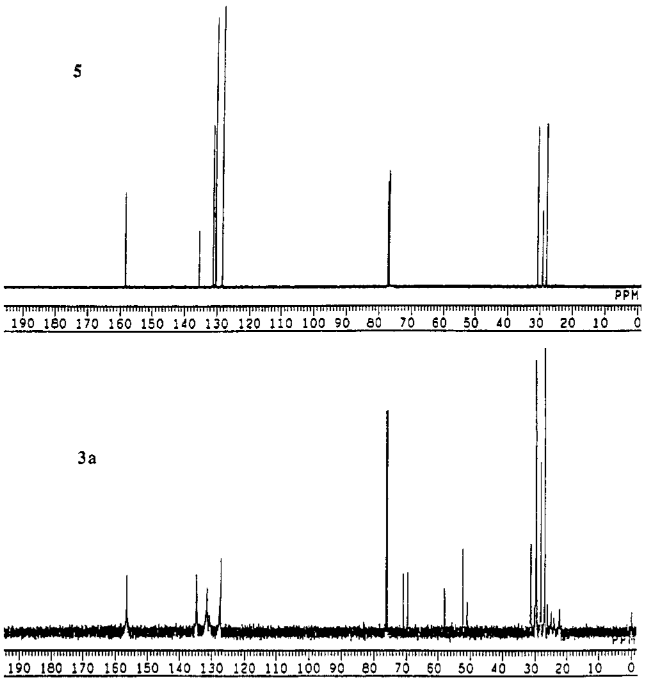
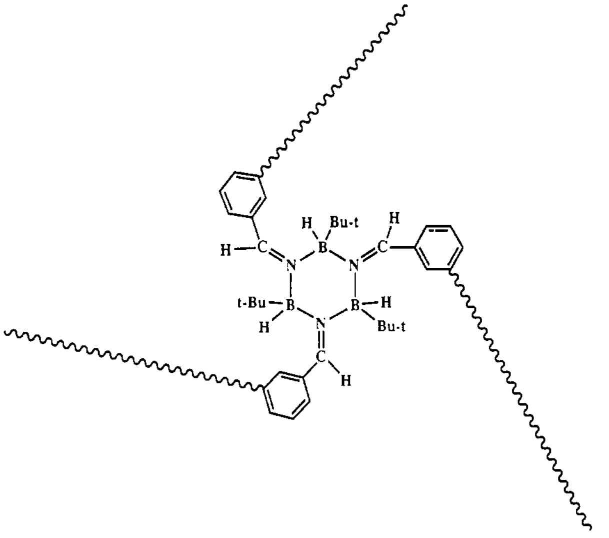


Figure 4. ^{13}C NMR spectra of **3a** and **5**.

Scheme IV



According to Hawthorne,[6] the iminoborane dimer (**4**) is decomposed into the corresponding benzaldehyde when **4** was refluxed with $H_2SO_4/EtOH/H_2O$ for 1 day. In the present study, the polymer **3a** did not produce isophthalaldehyde under the same reaction conditions. After the reaction, however, in its GPC analysis, the molecular weight of the polymer shifted to a lower molecular weight region. IR spectrum of the oligomer obtained showed a peak around 1700 cm^{-1}, indicating the presence of aldehyde groups.

TGA analysis of **3a** (Figure 6) shows that the weight loss started at 140 °C and was complete at 700 °C, forming a black solid (40%) under nitrogen flow. DSC was also measured under a nitrogen stream. At 200 °C, an irreversible exothermic peak was observed. After the measurement, the polymer became insoluble and no C═N was observed in its IR spectrum. This may be ascribed to the intermolecular reaction of C═N with B—H groups in the polymer structure.

Thermal stability in solution was also examined by monitoring the change of molecular weight in the GPC

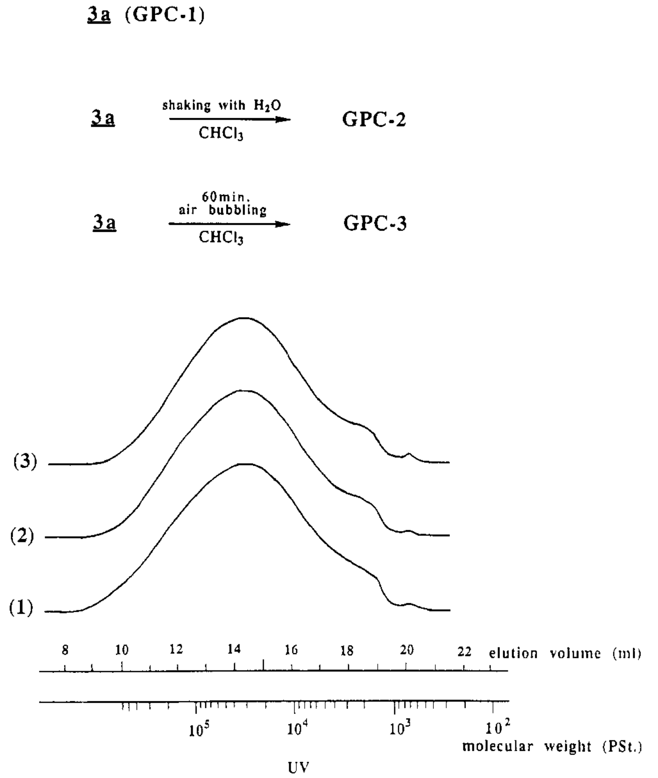


Figure 5. Stability of **3a** against air and moisture. (1) GPC trace of starting polymer. (2) After shaking with water for 2 days. (3) After air bubbling for 60 min.

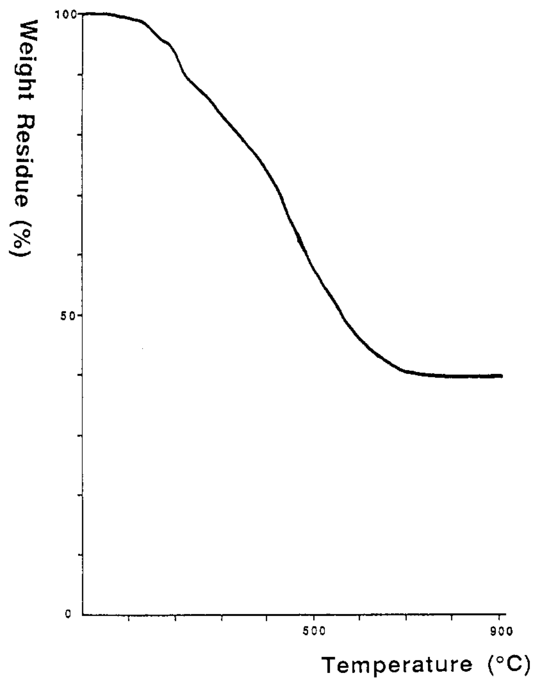


Figure 6. TGA trace of **3a**.

after heating a diglyme solution of **3a** at 100 °C under nitrogen (Figure 7). After 1 h, the peak became broader, and further heating formed mainly an insoluble material. This result may indicate the formation of some cross-linked materials. The molecular weight of the diglyme-soluble part was lower than that of the starting polymer. The IR spectrum of the obtained insoluble material was, however, identical with that of the starting soluble polymer. There are two possible explanations for the cross-linking reaction. One is an intermolecular reaction of C═N with B—H as discussed in the result of DSC, although the

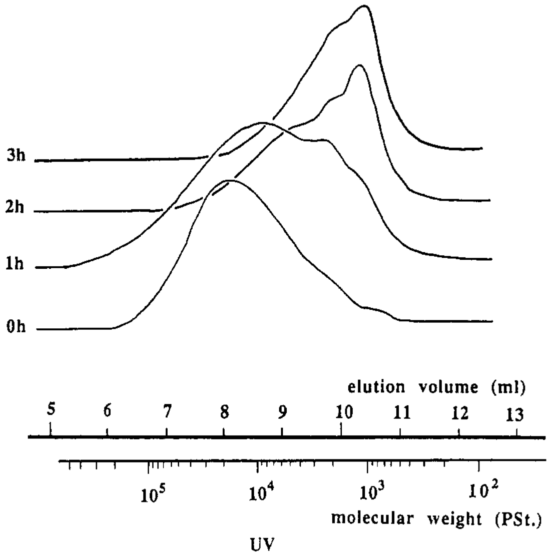


Figure 7. Thermal degradation of **3a** at 100 °C.

concentration of cross-linking reaction was too low to be detected by a spectroscopic method. Another possibility is the variation of a four-membered structure into a six-membered one in the polymer chain as was reported for the model compound (**5**) above its melting point.[6]

Experimental Section

Materials and Instruments. Diglyme and *N,N*-dimethylformamide (DMF) were dried over sodium and calcium hydride, respectively, and distilled before use. 4-Cyanophenol, 1,5-dibromopentane, ethanol, benzene, Na_2CO_3, and H_2SO_4 were used as received. **1** was prepared as reported earlier[14] and purified by distillation. **2a** and **2b** were recrystallized from ethyl acetate and methanol, respectively. **2d–f** were purified by distillation under reduced pressure.

^1H NMR spectra were recorded in $CDCl_3$ on a Hitachi R-600 instrument (60 MHz, tetramethylsilane as an internal standard). ^{11}B and ^{13}C NMR spectra were recorded in $CDCl_3$ on a JEOL JNM-JX-400 instrument ($BF_3 \cdot OEt_2$ and tetramethylsilane, external standard, respectively). IR spectra were obtained on a Perkin-Elmer 1600 spectrometer. UV spectra were measured on a Hitachi 200 UV–vis spectrophotometer. Gas chromatographic analyses were made on a Simadzu GC-6A instrument. Gel permeation chromatographic analyses were caried out on a Tosoh HLC-8020 instrument (TSK gel G3000, G4000, or Shodex AC804) 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) under air or nitrogen stream. Differential scanning calorimetry (DSC) was measured on a Seiko DSC200 instrument (10 °C/min).

Synthesis of Monomer 2c. To a 50-mL DMF suspension of 4-cyanophenol (2.4 g, 20 mmol) and Na_2CO_3 (2.9 g, 27 mmol, 0.991 equiv) was added 1,5-dibromopentane (2.4 g, 10 mmol), and the mixture was stirred for 6 h at 140 °C. The reaction mixture was reprecipitated into 300 mL of aqueous NaOH (1 N). The precipitated white solid was filtrated and washed with water and then with small amount of ethanol. Yield, 2.5 g (86%). Further purification was achieved by the recrystallization from ethyl acetate/*n*-hexane. **2c**: mp 112.5–113.5 °C; ^1H NMR ($CDCl_3$) δ 1.76 (CH_2, m, 6 H), 4.03 (OCH_2, m, 4 H), 6.77–7.77 (C_6H_4, m, 8 H); IR (KBr) 2955, 2876, 2221, 1606, 1509, 1471, 1301, 1262, 1173, 1007, 836, 715, 548 cm^{-1}.

Synthesis of 3a from 1 and 2a (Table I, Run 2). To a 4 M diglyme solution of **2a** (0.0579 g, 0.452 mmol) was added **1** (0.116 g, 0.896 mmol, 0.991 equiv) by using a microfeeder (it took 15 min to complete the addition) at 100 °C under nitrogen. After 1 h at that temperature, the reaction mixture was reprecipitated into 20 mL of $EtOH/H_2O$ (v/v = 1/1). The obtained polymer was freeze-dried with benzene. Yield, 0.116 g (96%). All the spectroscopic data of **3a** are given in Results and Discussion. In a similar manner, **3a** was prepared under various conditions. Table I, run 1: from 0.0702 g (0.548 mmol) of **2a** and 0.144 g (1.12 mmol, 1.02 equiv) of **1** at 80 °C. Table I, runs 3 and 4: from 0.241 g (1.88 mmol) of **2a** and 0.501 g (3.95 mmol, 1.05 equiv) of **1** for 2 and 4.5 h, respectively. Table I, run 5: from 0.0926 g (0.723 mmol) of **2a** and 0.183 g (1.42 mmol, 0.981 equiv) of **1** at 120 °C; yield 0.179 g (93%). Table II, run 1: from 0.102 g (0.795 mmol) of **2a** and 0.0648 g (0.502 mmol, 0.316 equiv) of **1**. Table II, run 2: from 0.118 g (0.924 mmol) of **2a** and 0.116 g (0.895 mmol, 0.49 equiv) of **1**. Table II, run 3: from 0.0642 g (0.501 mmol) of **2a** and 0.107 g (0.825 mmol, 0.823 equiv) of **1**. Table II, run 5: from 0.0436 g (0.340 mmol) of **2a** and 0.136 g (1.05 mmol, 1.55 equiv) of **1**; yield 0.0871 g (96%). Table II, run 6: from 0.0556 g (0.434 mmol) of **2a** and 0.243 g (1.884 mmol, 2.17 equiv) of **1**; yield 0.111 g (96%). Table II, run 7: from 0.0383 g (0.299 mmol) of **2a** and 0.229 g (1.78 mmol, 2.97 equiv) of **1**; yield 0.0782 g (98%).

Synthesis of 3b–f from 1 and 2b–f (Table IV, Runs 2–6). Similarly to **3a**, all the boron-containing polymers were prepared as follows. **3b** from 0.0481 g (0.375 mmol) of **2b** and 0.187 g (1.45 mmol) of **1**: yield 0.0847 g (84%); ^1H NMR ($CDCl_3$) δ 0.32–1.21 (CH_3, 18 H), 7.96 (C_6H_4, br s, 4 H), 8.41 (N=CH, br s, 2 H); IR (in $CHCl_3$) 2933, 2380, 1642, 1472, 1262, 1207, 1071, 804 cm^{-1}. **3c** from 0.0970 g (0.335 mmol) of **2c** and 0.150 g (1.16 mmol) of **1**: yield 0.131 g (93%); ^1H NMR ($CDCl_3$) δ 0.39–1.06 (CH_3, 18 H), 1.78 (CH_2, br m, 6 H), 4.09 (OCH_2, br m, 4 H), 6.73–8.06 (C_6H_4, m, 8 H), 8.26 (N=CH, br s, 2 H); ^{11}B NMR ($CDCl_3$) δ 5.1; IR (in $CHCl_3$) 2953, 2854, 2356, 1641, 1604, 1511, 1469, 1392, 1308, 1255, 1173, 1073, 1032, 959, 910, 834, 734 cm^{-1}. **3d** was prepared from 0.0498 g (0.0461 mmol) of **2d** and 0.105 g (0.817 mmol) of **1**. **3e** was prepared from 0.0312 g (0.229 mmol) of **2e** and 0.0551 g (0.427 mmol) of **1**. **3f** was prepared from 0.435 g (2.65 mmol) of **2f** and 0.705 g (5.46 mmol) of **1**.

Stability of 3a under Air. Air was bubbled into 1 mL of a chloroform solution of **3a** (0.01 g) for 1 h (120 mL/min). From the GPC measurement, no decrease of molecular weight was observed. All the spectroscopic data were identical with those for the starting polymer (**3a**). When a boron-containing polymer (**3a**) was kept under air for 1 month in the neat form, no change of molecular weight was observed in GPC measurement.

Stability of 3a in the Presence of Moisture. To 1 mL of a chloroform solution of **3a** (0.01 g), 1 mL of water was added under nitrogen, and the mixture was magnetically stirred for 2 days. From the GPC measurement, no decrease of molecular weight was observed. All the spectroscopic data were identical with those for the starting polymer **3a**.

Acid Hydrolysis of 3a. To a 1.2-mL solution of ethanol/H_2O (v/v = 1/3) were added 0.4 g of concentrated H_2SO_4 and then 0.2 g of **3a**. After being stirred under reflux for 1 day, the suspension was extracted with diethyl ether and concentrated. The IR spectrum of the product obtained showed a peak around 1700 cm^{-1} for aldehyde group. GPC analysis of the product showed lowering of the molecular weight (M_n = 490, M_w = 1220).

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References and Notes

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(11) In its IR spectrum, C═N and B—H stretching bands were somewhat weak in comparison with those of the polymer prepared at 100 °C as discussed later.

(12) Mp: 142.5–144 °C (lit.[6] mp 141–143 °C).

(13) The higher field shift in **3a** may arise from the torsion of structure, which is also observed in the UV measurement.

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Registry No. 1, 1184-67-4; **1/2a** (copolymer), 136893-04-4; **1/2b** (copolymer), 136893-05-5; **1/2c** (copolymer), 136919-99-8; **1/2d** (copolymer), 136893-06-6; **1/2e** (copolymer), 136893-07-7; **1/2f** (copolymer), 136893-08-8; **4**, 100-47-0; **5**, 100729-34-8; **6**, 108271-59-6; HOC_6H_4-*p*-CN, 767-00-0; $Br(CH_2)_5Br$, 111-24-0.