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Stable crosslinked π-conjugated boron containing polymers prepared by hydroboration polymerization or allylboration polymerization

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Summary

Stable crosslinked π-conjugated organoboron polymers and poly(cyclodiborazane)s were prepared by hydroboration polymerization or allylboration polymerization. The obtained gels, especially prepared by allylboration polymerization using 2,5-dicyanothiophene, 1,3,5-tricyanobenzene and triallylborane, showed good thermal stability and bathochromic shifts were observed in UV-vis absorption spectrum and the fluorescence emission spectrum, probably due to the interaction between polymer chains and more planer structure of crosslinked polymers.

Introduction

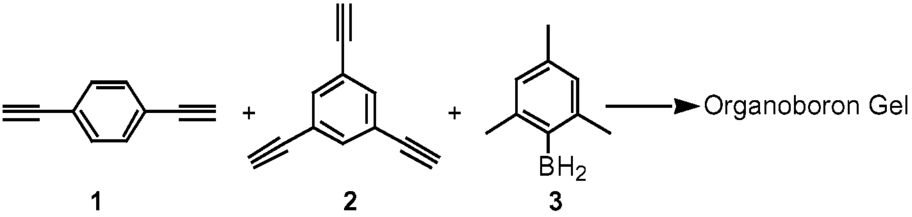
π-Conjugated polymers have attracted a great amount of attention owing to their optical properties. Though a lot of examples were reported about electron-rich p-type π-conjugated polymers, the number of reports on electron deficient n-type polymers was limited [1]. We have reported the syntheses of a novel type of n-type π-conjugated polymers - organoboron polymers - by hydroboration polymerization of aromatic diynes [2]. These polymers show interesting properties such as intense emission and excellent third-order nonlinear optical susceptibilities. In addition, π-conjugated poly(cyclodiborazane)s were also reported by our group [3]. Though fully aromatic poly(cyclodiborazane) prepared from terephthalonitrile and mesitylborane showed no evidence of extension of conjugation length, an incorporation of intramolecular charge transfer structure in the main chain brought about a dramatic change in the electronic structure of the polymer, and a bathochromic shift was observed in UV-vis absorption spectra.

As for π-conjugated polymer gel, environmental responses [4] and conductivity [5] of polythiophene gels were reported. In this paper, we report the preparation of π-conjugated crosslinked organoboron polymers and poly(cyclodiborazane)s by hydroboration polymerization or allylboration polymerization [6]. By introducing crosslinking structure in the polymer chains, more planer structure and more extended conjugation length would be expected. In addition, closely packed structure might improve the stability of organoboron polymers.

Results and discussion

Synthesis of π-conjugated crosslinked organoboron polymers by hydroboration polymerization using triethynylbenzene

First, we prepared organoboron gels by hydroboration polymerization of 1,4-diethynylbenzene (**1**) and 1,3,5-triethynylbenzene (**2**) using mesitylborane (**3**). **2** was prepared by the Pd/Cu catalytic reaction of 1,3,5-tribromobenzene with 3equiv of trimethylsilylacetylene and subsequent hydrolysis with NaOH. The preparation of organoboron gel was carried out in a similar way for π-conjugated organoboron polymers (Scheme 1) [2]. A THF solution of mesitylborane (**3**) was added to a THF solution of **1** and **2** and then the gelation took place soon when the concentration was high (runs 3-5 in Table 1). Under dilute conditions, the polymerization did not occur enough to form insoluble gels. The results are summarized in Table 1. Even in runs 3-5, the gelation was not completed due to the low reactivity and the soluble part in THF remained.



Scheme 1

Table 1. Synthesis of crosslinked organoboron polymers using triethynylbenzene

Run	**1** (mmol)	**2** (mmol)	**3** (mmol)	**1**:**2**	THF (ml)	Result
1	0.436	0.442	1.223	1:1.01	2.0	no gelation
2	0.160	0.649	1.134	1:4.05	2.0	no gelation
3	1.161	0.292	1.702	3.98:1	1.0	gelation
4	0.594	0.599	1.661	1:1.01	1.0	gelation
5	0.224	0.912	1.745	1:4.07	1.0	gelation

Because it is difficult to identify the structure of the insoluble part, the measurements of ^{1}H NMR, ^{11}B NMR spectra of the soluble part were carried out. The ^{11}B NMR spectrum showed one peak at 31.7 ppm, which is assignable to dialkenylborane unit [2] just as in the linear polymer. In the ^{1}H NMR spectrum, a peak owing to acetylene proton disappeared as in the case of the linear polymer. From these results, it is concluded that dialkenylborene units should exist in the insoluble parts.

Thermal stability and UV-vis absorption spectra of crosslinked organoboron polymers

To investigate the thermal stability of the organoboron gel, thermogravimetric analysis (TGA) of the gel was carried out. TGA of the corresponding linear polymer was also performed for comparison. As shown in Figure 1, the gel showed slower degradation than the linear polymer, which means better thermal stability of the gel compared with the linear polymer. This result would be explained by the rigid and crowded structure of the gel due to stronger intermolecular interactions.

Due to the difficulty of the measurement of UV-vis absorption spectra of the gels, the spectra of the soluble part in THF are shown instead. Table 2 describes absorption maxima of the polymers prepared from various ratios of **1** and **2**. The absorption maxima were observed between 350 nm and 380 nm, which indicates the extension of π-conjugation length. In addition, absorption maxima were hypsochromically shifted as the fraction of **2** increased. This result would be explained by assuming that π-conjugation is extended through *p*-substituted 1,4-divinylbenzene units and is not extended through *m*-substituted 1,3,5-trivinylbenzene structure. Though UV spectra of only soluble parts were examined here, it is expected that an extension of π-conjugation length also takes place in the organoboron gels. When a gel was immersed in THF for several weeks, it dissolved and became a homogeneous solution.

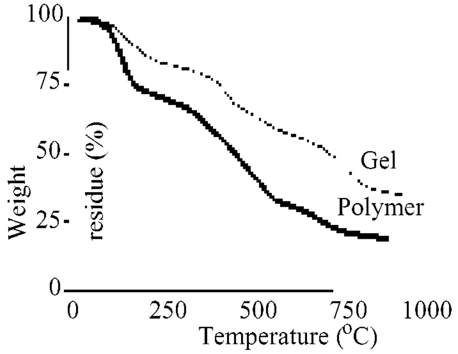


Figure 1. TGA traces of the organoboron gel and the linear polymer.

Table 2. Absorption maxima of crosslinked organoboron polymers

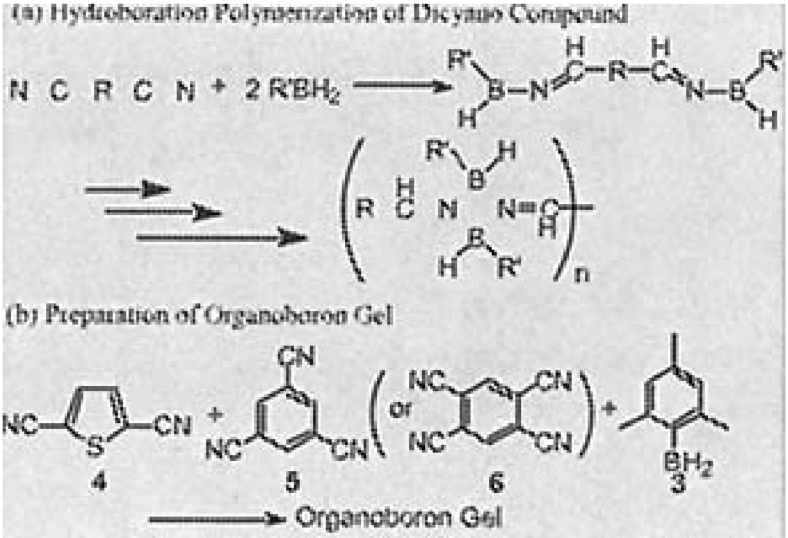
Run	**1**:**2**	λ_{max} (nm)
3	4:1	376
4	1:1	353
5	1:4	347
ref (linear)	1:0	399[a]

[a] Ref 2(a)

Synthesis of π–conjugated crosslinked poly(cyclodiborazane) by hydroboration polymerization using tricyanobenzene or tetracyanobenzene

The preparation of π-conjugated poly(cyclodiborazane) gels was also explored. The polymerization of dicyano compounds is a better way to obtain high molecular weight boron containing polymers than that of diyne compounds. The polymerization mechanism is shown in Scheme 2. Since the first step (addition of borane monomer to cyano group) is slow and the second step (dimerization of iminoboranes) is fast, the control of molar ratio of polymerization species would be easier. Therefore, preparation of stable gels would be possible by the polymerization of monomers bearing cyano groups.

The polymerizations were carried out by adding a THF solution of mesitylborane (**3**) to a THF solution of a mixture of 2,5-dicyanothiophene (**4**) and 1,3,5-tricyanobenzene (**5**) (or 1,2,4,5-tetracyanobenzene (**6**)). Table 3 shows the results of the polymerization. As in the case of organoboron gels described above, the gels were formed when the concentrations of the reaction mixtures were high, but the soluble parts partly remained. The polymerization using tetracyanobenzene (**6**) was also carried out in a similar way. The results are shown in Table 3.



Scheme 2

Table 3. Synthesis of crosslinked poly(cyclodiborazanes) by hydroboration polymerization using tricyanobenzene (**5**) or tetracyanobenzene (**6**)

Run	**4** (mmol)	**5** or **6** (mmol)	**3** (mmol)	**4**:**5** or **6**	THF (ml)	Result
1	0.165	0.165 (**5**)	0.902	1:1.00	1.0	Gelation
2	0.323	0.080 (**5**)	0.983	4.02:1	1.0	Gelation
3	0.394	0.040 (**5**)	0.995	9.90:1	1.0	No Gelation
4	0.201	0.198 (**5**)	1.104	1.01:1	2.0	Gelation
5	0.259	0.260 (**6**)	1.562	1:1.00	1.4	Gelation
6	0.527	0.133 (**6**)	1.574	3.96:1	1.4	Gelation
7	0.081	0.324 (**6**)	1.461	1:4.03	1.4	Gelation

UV-vis absorption spectra and fluorescence emission spectra of crosslinked poly(cyclodiborazane)s

Absorption maxima and emission maxima of the soluble parts are listed in Table 4. In absorption spectra, only run 2 showed explicit absorption maximum. This would be explained by the longer π-conjugation length of the gel in run 2 due to the higher ratio of **4**. On the other hand, these polymers showed similar photoluminescence spectra. The corresponding linear polymer (prepared from **3** and **4**) showed the absorption maximum at 364 nm and the emission maximum at 473 nm [3]. The blue shift of absorption maximum of crosslinked polymer might be explained by shorter conjugation length owing to the existence of *m*-substituted 1,3,5-tricyanobenzene in the polymer chains. The photoluminescence spectra of the gels were also measured here and a typical example is shown in Figure 2. Compared with those of soluble parts, the broad peaks were observed but emission maxima were not shifted drastically. This result might suggest that the intermolecular interactions are weak in the gels due to the existence of bulky side groups on cyclodiborazane moiety.

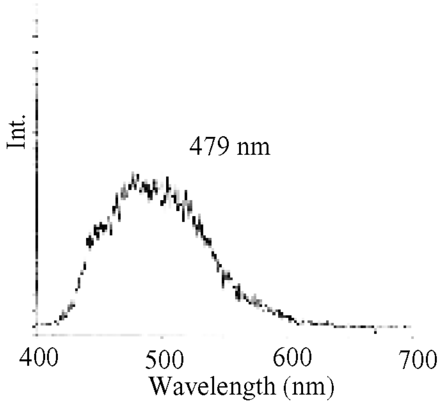


Figure 2. Fluorescence emission spectrum of poly(cyclodiborazane) gel (run 1, **4**:**5**=1:1) (swollen in THF, excited at 390 nm).

Table 4. Absorption maxima and emission maxima of crosslinked poly(cyclodiborazane)s by hydroboration polymerization

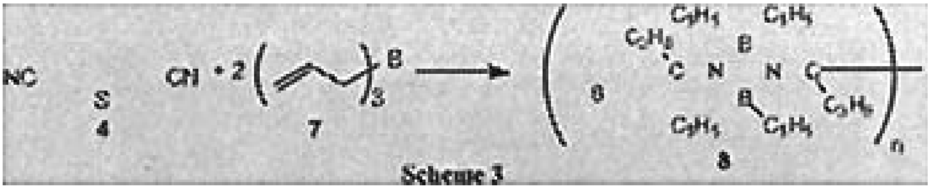
Run	**4**:**5**	UV λ_{max} (nm)^a	PL λ_{em} (nm)^a
1	1:1	335 (sh), 378 (sh)	447, 470
2	4:1	342, 380 (sh)	445, 471

^{a} In $CHCl_3$, r. t.
sh: shoulder

Preparation of π-conjugated poly(cyclodiborazane) and crosslinked poly(cyclodiborazane) by allylboration polymerization

As described above, even in the case of poly(cyclodiborazane) gels prepared from mesitylborane, a complete gelation is difficult and the formation of soluble part is inevitable. In order to avoid this problem, allylboration polymerization using triallylborane [6] was studied. As triallylborane is liquid, the polymerization can be carried out in bulk (without any solvent) and the reaction mixture was kept in high concentration. These conditions should lead to effective preparation of poly(cyclodiborazane) gels.

Before the preparation of the gel, we carried out allylboration polymerization using 2,5-dicyanothiophene (**4**) and triallylborane (**7**) to obtain a linear polymer for comparison (Scheme 3). Triallylborane was added to dicyanothiophene dropwise with stirring at 0 °C under nitrogen, and the reaction mixture became homogeneous and was stirred overnight. The molecular weight of the obtained polymer (M_n) was 1400 and the isolated yield was 86%.



Scheme 3

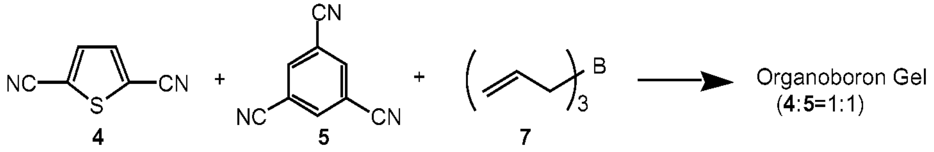
The results of UV-vis absorption are shown in Table 5. These spectra spectrum and fluorescence emission might support the extension of π-spectrum (excited at 320 nm) (in $CHCl_3$)

conjugation length as in the polymers prepared by hydroboration polymerization using mesitylborane.

Table 5. Absorption maxima and emission maxima of **8**

	UV λ_{max} (nm)	PL λ_{em} (nm)
solution	322	402
film	314, 323	404

The preparation of the gel was carried out in a similar way (Scheme 4). The obtained gel was subjected to the measurements of UV-vis and photoluminescence spectra after washing with THF. As shown in Figure 3, an absorption edge and the absorption maximum were shifted to longer wavelength region and the emission maximum was also bathochromic shifted. This result is different from that of the gels prepared by hydroboration polymerization using mesitylborane. It would be explained by the stronger interaction between polymer chains. The cyclodiborazane moiety bearing allyl groups might be less bulky and the stronger interaction should be possible. In addition, the polymer chain might be more planer due to the stronger interaction, and these factors might lead to the red shift in UV-vis spectrum and PL spectrum.



Scheme 4

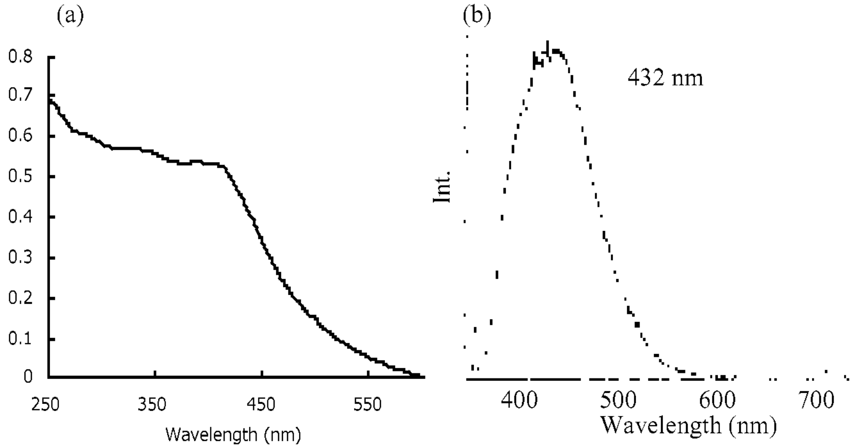


Figure 3. UV-vis absorption spectrum (a) and fluorescence emission spectrum (excited at 360 nm) (b) of the poly(cyclodiborazane) gel prepared by allylboration polymerization.

The thermal stability of the gel was demonstrated by TGA in Figure 4. The higher stability of the gel was confirmed by comparing T_{10} (the temperature at which 10% weight loss occurs) of the gel and the corresponding linear polymer.

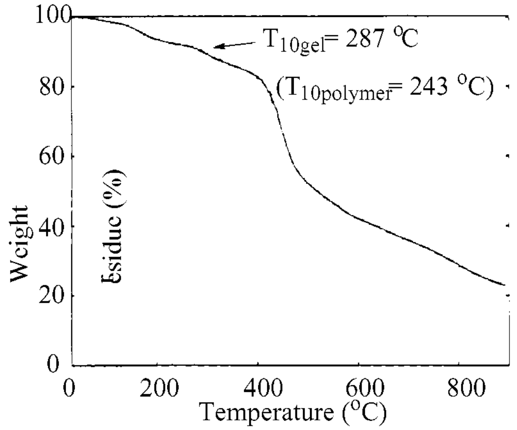


Figure 4. TGA trace of the poly(cyclodiborazane) gel prepared by allylboration polymerization.

Conclusion

We disclosed the preparation of π-conjugated crosslinked organoboron polymers in this paper. Due to low degree of polymerization, the complete gelation and formation of insoluble gels were difficult, but the polymerization behavior was improved by using different monomer or carrying out polymerization in bulk. From the results of TGA, the gels were found to show better thermal stability compared with the corresponding linear polymers. In addition, the gel prepared by allylboration polymerization showed bathochromic shift in UV-vis absorption spectrum and fluorescence emission spectrum. These gels could be expected as a novel type of optical materials because of their emission properties and improved stabilities.

Experimental section

Materials and instruments

Tetrahydrofuran was dried over sodium and distilled before use. Mesitylborane was prepared by the modified procedure [7] of the reported method [8]. Triallylborane was prepared according to the reported procedure [9]. 1,4-Diethynylbenzene was purified by sublimation. 1,3,5-Triethynylbenzene was prepared from 1,3,5-tribromobenzene according to the reported procedure [10] and purified by sublimation. 2,5-Dicyanothiophene was synthesized by the cyanidation [11] of 2,5-dibromothiophene. Other chemicals were all used as received.

^1H NMR and ^{11}B NMR spectra were recorded in $CDCl_3$ on a JEOL EX-270 instrument. UV-vis absorption spectra were recorded on a JASCO V-530 spectrophotometer. Fluorescence emission spectra were recorded on a Perkin-Elmer LS50B luminescence spectrometer. Thermogravimetric analyses (TGA) were made on a Seiko TG/DTA 6200 (10 °C/min).

*Preparation of crosslinked organoboron polymers by hydroboration polymerization using **1**, **2** and **3***

A typical example of polymerization is as follows: To a THF (0.5 ml) solution of 1,4-diethynylbenzene (**1**) (28.3 mg, 0.224 mmol) and 1,3,5-triethynylbenzene (**2**) (137.0 mg, 0.912 mmol) was added a THF (0.5 ml) solution of mesitylborane (**3**) (230.3 mg, 1.745 mmol) dropwise at 0 °C under nitrogen. Gelation occurred soon and the reaction mixture was freeze-dried with benzene. The polymeric material was obtained quantitatively. The gel was purified by washing with THF.

*Preparation of crosslinled poly(cyclodiborazane)s by hydroboration polymerization using **3**, **4** and **5***

A typical example of polymerization is as follows: To a THF (0.5 ml) solution of 2,5-dicyanothiophene (**4**) (43.3 mg, 0.323 mmol) and 1,3,5-tricyanobenzene (**5**) (12.3 mg, 0.0803 mmol) was added a THF (0.5 ml) solution of mesitylborane (**3**) (129.8 mg, 0.983 mmol) dropwise at 0 °C under nitrogen. Gelation occurred within few minutes after the completion of the addition. The obtained gel was washed with THF. Isolated yield was 89%.

*Preparation of crosslinked poly(cyclodiborazane) by allyboration polymerization using **4**, **5** and 7*

Triallylborane (7) (218.0 mg, 1.63 mmol) was added to a mixture of 2,5-dicyanothiophene (**4**) (40.4 mg, 0.301 mmol) and 1,3,5-tricyanobenzene (**5**) (45.9 mg, 0.300 mmol) dropwise at 0 °C under nitrogen. Gelation occurred soon and the obtained gel was washed with THF. Isolated yield was 39%.

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