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# Boration Copolymerization between Diynes and Diisocyanates. Novel Alternating Copolymerization Strategy

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Synthesis of polymeric inorganic materials has been a subject of strong interest over the past decades, as represented by polysiloxanes,[1] polyphosphazenes,[2] polysilanes,[3] metallocene-based polymers,[4] and rigid rod polymers.[5] Incorporation of inorganic elements into a main chain of polymers might be a promising way to obtain materials having unique mechanical, electrical, and optical properties.

Recently, we have reported novel methodologies to obtain organoboron main chain polymers by means of hydroboration polymerization.[6] These novel types of reactive polymers are interesting not only as polymeric precursors for the functionalized carbon-backbone polymers[7] but also as a new class of boron-containing materials. Especially, poly(cyclodiborazane)s prepared by hydroboration polymerization of dicyano compounds (Figure 1a)[8] and the polymers prepared by phenylboration polymerization of diynes[9] (Figure 1b) exhibit relatively high stability against air and thermal oxidation. Furthermore, we reported that haloboration polymerization of diynes or haloboration−phenylboration polymerization of diisocyanates also gave the corresponding organoboron polymers having bis($\beta$-haloalkenyl)borane units[10] or diamidoborane units,[11] respectively (Figure 1c,d). Here we report a novel alternating boration copolymerization strategy to obtain organoboron polymers having monomeric iminoborane units in their main chain,[12] in which a boron−nitrogen bond can be incorporated in the conjugation path.

Alternating boration copolymerization was achieved by utilizing the different boration reactivities between acetylene and isocyanate. Haloboration of aromatic acetylene bonds takes place under mild reaction conditions (−78 °C∼), while the phenylboration reaction requires severe reaction conditions (70 °C∼).[13] On the other hand, both haloboration and phenylboration of isocyanates proceed smoothly at room temperature.[11] Accordingly, the treatment of an aromatic diyne monomer with 2 molar equiv of diphenylbromoborane (**1b**) (selective haloboration reaction toward the acetylene bond) and subsequent reaction with an equimolar amount of diisocyanate would give a polymer having the alternating unit structure (Scheme 1b).

First, haloboration−phenylboration copolymerization among diynes (**2**), diisocyanates (**3**), and phenyldichloroborane (**1a**) by simultaneous feeding of monomers was examined (Scheme 1a). A typical procedure is as follows. To a 1.0 M solution of **1a** in chloroform, a half molar amount of tolylene-2,4 diisocyanate (**3a**), and 1,9-decadiyne (**2b**) were added at room temperature under nitrogen. After stirring for 24 h, the reaction mixture was poured into *n*-hexane. The obtained brown powder was dissolved in THF and was subjected to GPC measurement. The results of polymerization using various combinations of monomers are summarized in Table 1. When 1,4-diethynylbenzene (**2a**) was employed as a diyne monomer, no copolymer was obtained. In the polymerization using **2b**, the corresponding copolymers were obtained. However, the content of the unit (estimated from $^1$H NMR) originating from the diyne monomer was much lower than expected from the feed ratio, probably due to the relatively low reactivity of the diyne monomers.

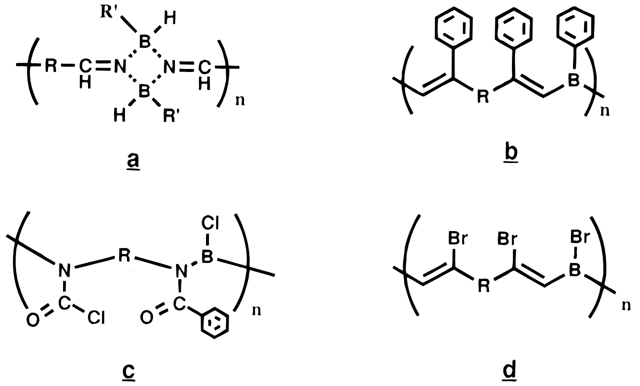
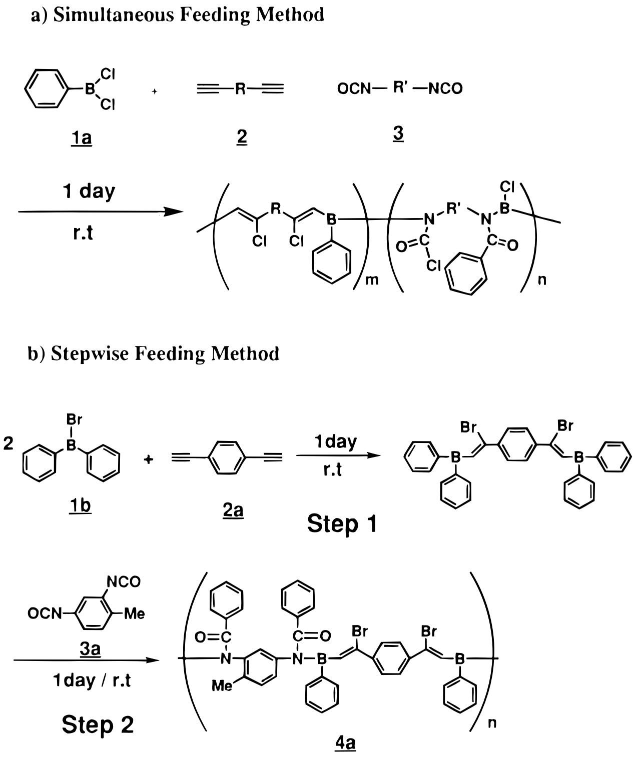


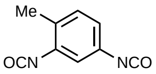
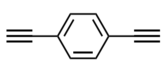
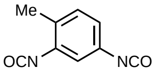
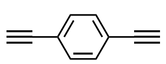
**Figure 1.** Examples of organoboron polymers produced by boration polymerization.

**Scheme 1**



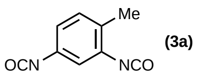
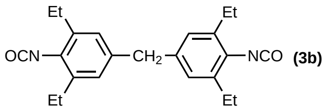
To obtain copolymer having a higher content of alkenylborane unit and alternating unit structure, the stepwise polymerization method was examined (Scheme 1b). In the first step, 2 molar equiv of **1b** was added to a 1.0 M chloroform solution of **2a** at room temperature under nitrogen and the reaction mixture was stirred for 24 h. From the $^1$H NMR spectrum, disappearance of the acetylene proton (3.22 ppm) was observed. In the second step, an equimolar amount of **3** was added very

**Table 1. Boration Copolymerization of Diyne (2) and Diisocyanate (3) with PhBCl$_2$ (1a)[a]**

| run | 2 | 3 | feed ratio (**1a**/**3**/**2**) | $M_w$[b] | $M_n$[b] | $M_w/M_n$[b] | polymer[c] content (**3**/**2**) | yield (%)[d] |
|---|---|---|---|---|---|---|---|---|
| 1 | $\equiv$—(CH$_2$)$_6$—$\equiv$ |  | 1.0/0.58/0.52 | 2600 | 2000 | 1.83 | 79/21 | 75.3 |
| 2 |  |  | 1.0/0.50/0.50 | | | no polymerization | | |
| 3 |  | OCN(CH$_2$)$_6$NCO | 1.0/0.52/0.51 | 6000 | 3600 | 1.68 | 100/0 | |
| 4 | $\equiv$—(CH$_2$)$_6$—$\equiv$ | OCN(CH$_2$)$_6$NCO | 1.0/0.51/0.51 | 5200 | 4100 | 1.27 | 87/13 | 74.9 |

[a] Reactions were carried out by adding **1a** to a CHCl$_3$ solution of **2** and **3** at room temperature. [b] GPC (THF), polystyrene standards. [c] All the polymer contents were determined by $^1$H NMR spectra. [d] Isolated yields after reprecipitation into *n*-hexane.

**Table 2. Alternating Boration Copolymerization of 1,4-Diethynylbenzene (2a) and Various Diisocyanates (3) with Ph$_2$BBr (1b)[a]**

| run | 3 | feed ratio (**1b**/**3**/**2**) | $M_w$[b] | $M_n$[b] | $M_w/M_n$[b] | yield (%)[c] |
|---|---|---|---|---|---|---|
| 1 |  | 1.0/0.51/0.48 | 13600 | 4300 | 3.17 | 74.5 |
| 2 |  | 1.0/0.48/0.50 | | no polymerization | | |
| 3 | OCN(CH$_2$)$_6$NCO (**3c**) | 1.0/0.58/0.52 | 4600 | 2600 | 1.78 | 71.9 |
| 4 | OCN(CH$_2$)$_{12}$NCO (**3d**) | 1.0/0.54/0.51 | 4600 | 2500 | 1.86 | 68.2 |

[a] Step 1 was carried out by adding **1b** to CHCl$_3$ solution of **2a** at room temperature. Step 2 was performed by adding **3** to the resulting solution of Step 1. [b] GPC (THF), polystyrene standards. [c] Isolated yields after reprecipitation into *n*-hexane.

slowly and the reaction mixture was stirred for another 24 h. After evaporation of the solvent, the obtained brown gum was reprecipitated from chloroform into *n*-hexane. The polymers prepared were soluble in common organic solvents such as THF, chloroform, DMSO, and DMF. However, when too much **3** was fed, or **3** was fed too rapidly, sometimes gelation was also observed. The results of alternating boration copolymerization using various diisocyanates are listed in Table 2. Except for the case of run 2, the corresponding polymers (**4**) were obtained. The relatively higher estimation of molecular weight of the polymer prepared in run 1 might be due to the rigid backbone structure in comparison with those prepared in runs 3 and 4.

The structures of the polymers were supported by $^1$H NMR, $^{11}$B NMR, and IR spectra. In the IR spectra, the peak due to N=C=O streching at 2262 cm$^{-1}$ disappeared while the C=O streching of the amide group at 1707–1715 cm$^{-1}$ appeared. The extent of unit alternation can be clearly monitored by $^{11}$B NMR spectra. As shown in Figure 2, in the $^{11}$B NMR spectrum of the polymer prepared from 1,6-hexamethylene diisocyanate (**3c**) and **1a**, the main peak appears at 4.7 ppm (diamidoborane) and that of the polymer prepared from **2a** and **1a** appears at 60.5 ppm (bis($\beta$-haloalkenyl)borane). In comparison with those chemical shifts, that of polymer **4a** (produced from **2a** and **3a**) is located almost in the midpoint of those two polymers, at 29.2 ppm (($\beta$-haloalkenyl)amidoborane). This result suggests a highly alternating nature of the polymerization system. The small peak at 0.55 ppm might correspond to diamidoalkenylborane, possibly formed by further phenylboration reaction of the B–Ph moiety with isocyanate (cross-linking reaction).

To investigate the air stability of the polymer **4a**, an air-bubbling experiment was carried out in THF solution. From the GPC traces, significant degradation of the polymer was not observed even after air bubbling for 5 days.

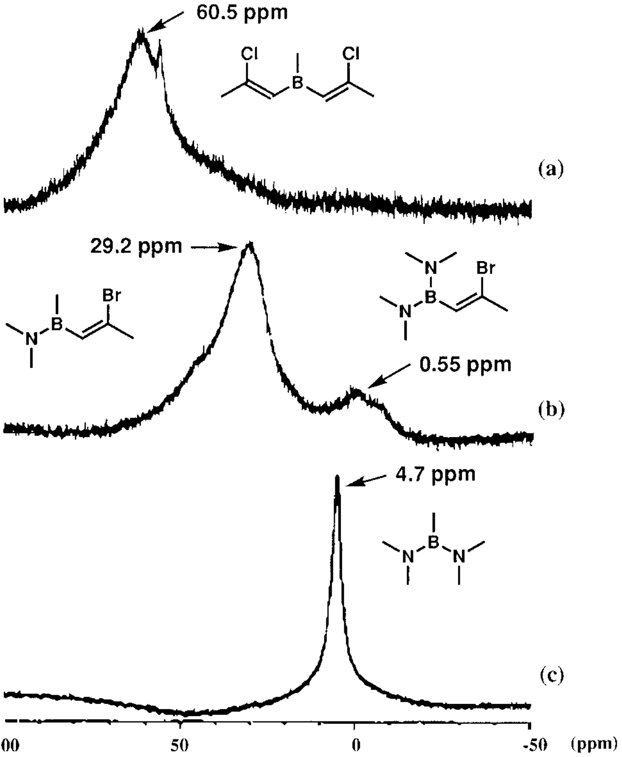


**Figure 2.** $^{11}$B NMR spectra of organoboron polymers prepared by boration polymerization: (a) haloboration polymerization between **1a** and **2a**; (b) haloboration–phenylboration alternating copolymerization between **2a** and **3a** using **1b**; (c) haloboration–phenylboration polymerization between **1a** and **3c**.

In conclusion, an alternating haloboration−phenylboration copolymerization methodology was explored by taking advantage of different boration reactivities between diynes and diisocyanates. The polymers obtained possess monomeric iminoborane in their main chain, and those prepared from aromatic monomers showed high air stability. In addition, **4a** can be regarded as a novel type of conjugated polymer, since the B−N bonds have some double bond nature due to the well-established $p\pi-p\pi$ interaction.[14] Therefore, further studies on its physical properties would be also interesting.

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