Synthesis of π-Conjugated Poly(cyclodiborazane)s by Organometallic Polycondensation

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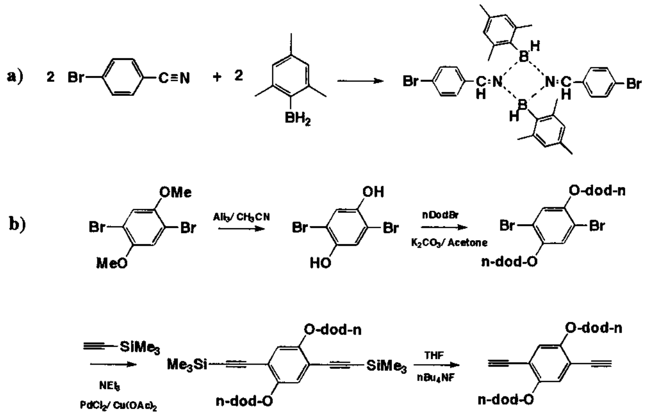
ABSTRACT: Donor−acceptor type π-conjugated poly(cyclodiborazane)s were synthesized by organometallic polycondensation between cyclodiborazane-containing dibromide and 2,5-didodecyloxy-1,4-diethynylbenzene utilizing Sonogashira coupling. The polymerization was carried out under a nitrogen atmosphere, in THF/NEt$_3$ solution in the presence of a catalytic amount of copper acetate, palladium chloride, and triphenylphosphine at 80 °C for 12 h. After reprecipitation into MeOH, the resulting polymer was isolated as a brown powder in moderate yield. The polymer obtained was soluble in common organic solvents such as THF, chloroform, and benzene, and its structure was confirmed by ^{1}H NMR, ^{11}B NMR, and IR spectra. The number-average molecular weight of the polymer was 8500 from the gel permeation chromatographic analysis (GPC, THF, PSt standards). In the UV−vis absorption spectrum recorded in chloroform, the absorption maximum was observed at 414 nm, owing to extension of π-conjugation via the vacant p-orbital of the boron atom and intramolecular charge transferred structure. This polymer exhibited an intense blue-green light emission upon irradiation at 414 nm.

Organometallic polycondensation[1] has been one of the most common methods for the preparation of π-conjugated polymers whose molecular weights are sufficiently high to exhibit their characteristic optical or electric properties. Especially, palladium- or nickel-catalyzed polymerization utilizing Suzuki coupling, Stille coupling, Sonogashira coupling, etc., had also enabled the alternating unit arrangement, which led to the generation of polymers having intramolecular charge transferred structure,[2] regioregular poly(alkylthiophene)s,[3] poly(arylene−ethynylene)s,[4] and so on.

Here is examined a synthesis of donor−acceptor type π-conjugated poly(cyclodiborazane)s[5] by polycondensation between cyclodiborazane-containing dibromide and 2,5-didodecyloxy-1,4-diethynylbenzene to afford successfully the corresponding polymer in moderate yield. Generally, organoboron compounds tend to retard the nickel- or palladium-catalyzed cross-coupling reaction; however, transmetalation appears to be suppressed in the present system presumably owing to high steric hindrance around the boron atom or specific electronic state of boron atom.

We have recently reported that hydroboration polymerization between aromatic diyne with mesitylborane gave π-conjugated organoboron polymers via the vacant p-orbital of the boron atom.[6] The fully aromatic poly(cyclodiborazane)s[7] should be also regarded as π-conjugated polymer via the boron atom; however, poorly extended π-conjugation was implied in the UV−vis absorption spectrum of the polymer derived from 1,4-dicyanobenzene. Nevertheless, the presence of charge transferred structure affected dramatically on the electronic state of the polymer, leading to the bathochromic shifted absorption to the visible region.[5] In the present system as well, the polymer obtained acted as organoboron π-conjugated polymers in their optical or electrochemical behavior.

Scheme 1



The cyclodiborazane containing dibromide was prepared by hydroboration of 4-bromobenzonitrile (**1**) with an equivalent of mesitylborane (Scheme 1a). 2,5-Didodecyloxy-1,4-diethynylbenzene (**2**) was prepared according to the reported method,[8] as depicted in Scheme 1b. The polymerization between **1** and **2** was performed in THF/NEt$_3$ solution in the presence of a catalytic amount of copper acetate, palladium chloride, and triphenylphosphine (Scheme 2). After stirring the reaction mixture for 12 h at 80 °C under a nitrogen atmosphere, the obtained crude polymer was purified by reprecipitation into MeOH to give the polymer **3** as a brown powder in 47% yield. **3** was soluble in common organic solvents such as THF, chloroform, and benzene. The gel permeation chromatographic analysis (GPC, THF, PSt standards) showed that the number-average molecular weight of **3** corresponds to 8500. The polymerization using a cyclodiborazane monomer prepared from tripylborane was also examined in a similar manner; however, the majority of the products was insoluble probably due to much poor solubility of the cyclodiborazane monomer.

The structure of **3** was supported by ^{1}H NMR, ^{11}B NMR, and IR spectra. In the ^{1}H NMR spectrum of **3**, the imine proton which is characteristic for cyclodiborazane formation was observed at 7.95 ppm, in addition to the peaks owing to mesityl group at 2.25 and

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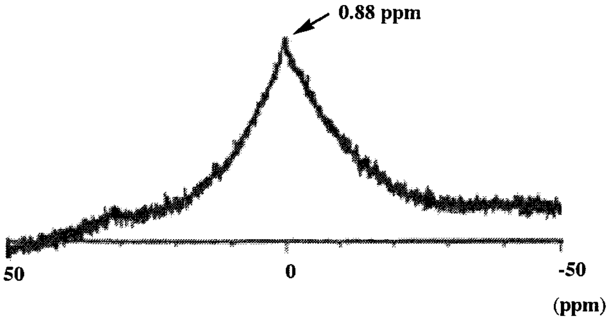


Figure 1. ^{11}B NMR spectrum of **3** in CDCl$_3$.

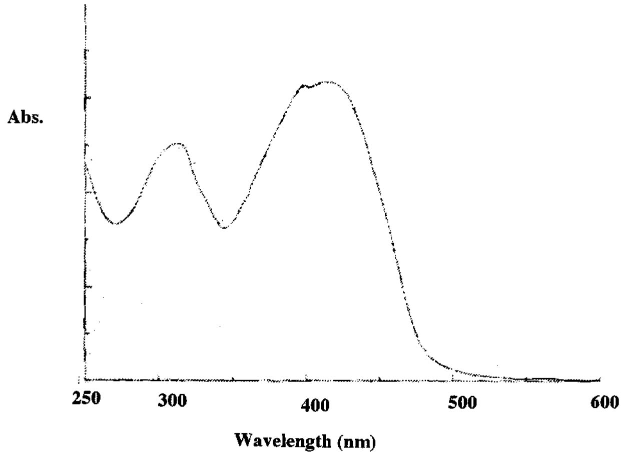


Figure 2. UV−vis absorption spectrum of **3** in chloroform at room temperature.

6.86−6.94 ppm. The ^{11}B NMR spectrum of **3** recorded in CDCl$_3$ (Figure 1) showed only one peak at 0.88 ppm, indicating that typical cyclodiborazane structure is present[7a−d] and that the structure was not affected by the polymerization condition where organometallic catalysts were employed. As mentioned before, this result proposes that transmetalation should be retarded in this system possibly owing to high steric hindrance around the boron atom or specific electronic state of the boron atom. It should be also noted that no peak assignable to monomeric iminoborane (around 30 ppm) was observed in this spectrum. Generally, in the case of hydroboration polymerization of dicyano compounds, the formation of monomeric iminoborane or borazine structure as structural defect is unavoidable. In the present system, however, the polymerization of purified cyclodiborazane monomer **1** resulted in the formation of the polymer **3**, free of such structural defects. In the IR spectrum of **3** sharp absorption peaks owing to the stretching of B−H bond (2398 cm^{-1}), triple bond (2205 cm^{-1}), and C=N bond (1646 cm^{-1}) were observed.

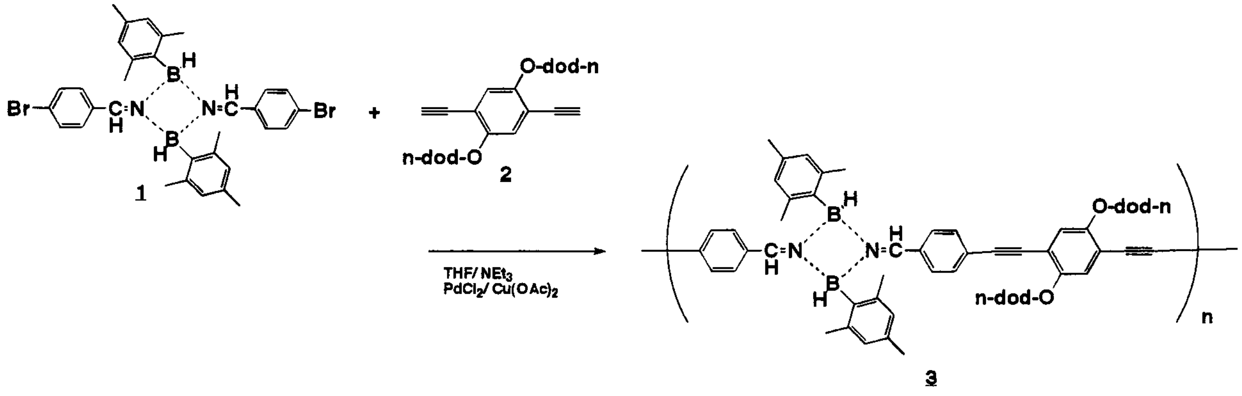
The polymer **3** exhibited essentially a similar optical behavior as those prepared by hydroboration polymerization.[5] The UV−vis absorption spectrum of **3** was recorded in chloroform at room temperature, as represented in Figure 2. In this spectrum, the absorption maximum was observed at 414 nm as a consequence of extension of π-conjugation length via the vacant p-orbital of the boron atom and also of intramolecular charge transferred structure due to the alternating arrangement of donor and acceptor units.

The fluorecence emission spectrum of **3** (in chloroform at room temperature; excitation wavalength at 414 nm) exhibited an intense emission peak at 466 nm, which resulted in the observation of blue-green light emission. The location of the emission maximum showed a slight dependence on kind of solvents. For instance, relatively blue-shifted emission ($\lambda_{\max}$ 458 nm) was observed in less polar Et$_2$O, while **3** showed red-shifted emission in polar DMF ($\lambda_{\max}$ 474 nm). This result implies the presence of intramolecular charge transferred structure, as was also found in the previous system.[5]

A cyclic voltammogram of **3** was recorded in 0.1 M THF solution of tetra-*n*-butylammonium perchlorate versus Ag/Ag$^+$ (sweep rate = 100 mV/s). **3** was found to be electrochemically active toward n-doping, showing a reduction peak at −1.76 eV owing to high electron affinity of the organoboron unit. A reoxidation peak was also observed at −1.14 eV. The relatively large peak potential difference between n-doping and n-undoping peak might be explained by assuming some structural change during the cycle. Although reduction peak intensity of **3** had slightly decreased and reoxidation peak had increased during the repeated scanning, essentially reversible cycles were observed. The reduction and reoxidation peak potentials of **3** were found to be almost independent of the sweeping rate in the range 10−100 mV, while peak intensities were enhanced as increasing the sweep rate. This also supports the reversible nature of the system. Because of the highly electron-accepting property of the cyclodiborazane unit, **3** was almost intact toward oxidation until +0.83 V, where irreversible oxidation peak started.

The stability of **3** was assessed by an air-bubbling experiment and treatment of **3** with water. After a stream of air was vigorously bubbled into a THF solution of **3** for 24 h, the changes in the molecular weights were monitored by GPC measurement. During the measurement, no significant change in GPC trace

Scheme 2



of **3** was observed, suggesting the fairly high stability of **3** against air. Similarly, after the treatment of **3** with water for 24 h, no decrease in the molecular weight of **3** was observed.

Supporting Information Available: Experimental section, fluorescence emission spectrum of **3**, cyclic voltammogram of **3**, plot showing the stability of **3**, and table showing the dependence of the first reduction potential of **3** on sweep rate. This material is available free of charge via the Internet at http://pubs.acs.org.

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